



Australian Colloid and Interface Symposium

**Crowne Plaza Hotel
Coogee Beach, Sydney**

4–8 February, 2007

Program and Abstracts

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Cover graphics. The background illustration used for the cover (and other ACIS-2007 publicity material) is an optical micrograph showing the lamellar phase of egg-yolk lecithin mixed with water. The use of crossed polarisers highlights the anisotropic liquid crystalline phase while isotropic regions remain dark. Photograph courtesy of Damyanti Sharma; graphical layout courtesy of Baden Smith.

Welcome and Introduction

It is my pleasure, as Chair of the Organising Committee, to welcome you to the Australian Colloid and Interface Symposium 2007. This is the third in a series of biennial conferences held at Coogee, one of Sydney's glorious suburban beaches. We hope that you will enjoy several days of discussing top-quality science, and we also hope that you enjoy your visit to this wonderful venue.

The main purpose of ACIS is to serve as the national meeting for the Australian colloid and surface science community. Following the success of the previous ACIS meetings in 2003 and 2005, we are also seeing a large amount of interest from overseas. In fact almost 40% of our delegates are international visitors, coming from 16 different countries. It is also very pleasing to have a healthy number of delegates from industry.

The level of interest in ACIS 2007 has created one little problem, although as a few people have remarked, it is a nice problem for the conference organisers to have. There was an overwhelming response to our call for abstracts for this meeting, and we have been unable to fit all of the requested talks into the program. We stretched the program to the limits of time and tolerance, but even so, there are a number of authors who will present their work as a poster when they would have preferred an oral presentation. Our apologies to those people, but we trust that everyone will appreciate the high quality of talks and posters to be presented over the next few days, even if it does make for a crowded program.

The program has been arranged into a number of themes, each organised by two or three volunteers whose names are listed overleaf. We are deeply grateful to them, and to the theme sponsors, for making such a strong program possible. A particular feature of ACIS 2007 is that one of the themes honours the work of Professor Jacob Israelachvili. I am not sure whether this is closer to his 60th or his 65th birthday celebrations, but in any case his friends in Australia want to take this opportunity to celebrate his numerous contributions to colloid and surface science. Much of that work has its origins in Jacob's halcyon days at the Australian National University in the late 1970's and early 1980's.

In addition to the theme chairs and sponsors, bucketloads of thanks are due to our other sponsors whose logos appear on the back cover; to Baden Smith for his graphics work; to Kathryn Prohaska for her work particularly with compiling this book; to Tim Barnes for agreeing to be official photographer; to the cable guy Craig Hackney for looking after AV matters; to Jane Yeaman from Tulips Meetings Management who has looked after countless details of the conference organisation; and above all to my colleagues on the conference organising committee. I had little to do apart from arrange several phone hook-ups, while Erica, Gayle, Jamie, Pat and Russell, using their experience and expertise from previous ACIS meetings, arranged the various aspects required to organise a successful conference. I believe they have done a great job; now it's over to you, the participants, to make the conference memorable scientifically and enjoyable in all aspects.

Roger Horn

Chair, Organising Committee
ACIS 2007

Organising Committee

Prof. Roger Horn	University of South Australia	Chair
Dr. Erica Wanless	University of Newcastle	Secretary
Dr. Gayle Morris	Victoria University	Treasurer
Dr. Jamie Schulz	ANSTO	Webmaster and Local Coordinator
Dr. Patrick Hartley	CSIRO Molecular & Health Technologies	Sponsorship Coordinator
Prof. Russell Crawford	Swinburne University of Technology	Posters and Social Program
Ms. Jane Yeaman	Tulips Meetings Management	Conference Organiser

Theme Chairs

SPECTROSCOPY AND SCATTERING IN SURFACE AND COLLOID SCIENCE

Dr. David Beattie	University of South Australia
A/Prof. Jim McQuillan	University of Otago, NZ

SURFACE FORCES, NANOTRIBOLOGY AND BIOLOGICAL INTERACTIONS

A/Prof. Michelle Gee	University of Melbourne
Prof. Roger Horn	University of South Australia

INORGANIC OXIDE SURFACES

A/Prof. George Franks	University of Melbourne
A/Prof. Jonas Addai-Mensah	University of South Australia
Dr. Yang Gan	University of Newcastle

DROPS AND BUBBLES

Dr. Ray Dagastine	University of Melbourne
Prof. Clive Prestidge	University of South Australia

HIERARCHICAL MATERIALS

Dr. Calum Drummond	CSIRO Molecular & Health Technologies
Prof. Matt Trau	University of Queensland

FRONTIERS OF COLLOID AND INTERFACE SCIENCE

Dr. Shannon Notley	Australian National University
Dr. Rob Atkin	University of Sydney
Prof. Greg Warr	University of Sydney

PHARMACEUTICAL APPLICATIONS

Dr. Ben Boyd	Monash University
Dr. Ian Larson	Monash University

General Information

Name Badges

Please wear name badges to all sessions and social events. Name badges are your ticket of admittance to all sessions and social programs. Accompanying guests also need to wear name badges to social events they have been booked in to.

Abstract Books

A limited number of additional copies of the Conference Abstract Book are available from the registration desk from Tuesday onwards at a cost of \$33 each, should you decide to purchase an additional copy.

PowerPoint Presentations

Talks (apart from Keynote and Plenary talks) will be a total of 20 minutes (15 minutes + 5 minutes for questions). If you are presenting an oral presentation, please bring your PowerPoint presentation with you on a CD or USB/memory stick. You will be able to load your own presentation in the break preceding your session.

Poster Presentations

If you are presenting a poster presentation, please bring your poster and velcro with you on Monday morning and you will have the opportunity to put your poster up before the sessions start on Monday. Please review the abstract book to determine your abstract number before placing it in the correct location no later than lunchtime on Monday. You will need to stand at your poster during Monday night's poster session, odd numbers from 6:00pm-7:00pm and even numbers from 7:00pm-8:00pm. You are encouraged to leave your poster up during sessions on Tuesday, however your poster **MUST** be removed before the drinks break on Tuesday afternoon (3:30pm). Posters should be 'A0' in size (approximately 900 mm wide x 1200 mm high).

Message Board

A message and notice board will be located adjacent to the registration desk throughout the conference. Emergency phone messages can be left by phoning 0408 498860. Please check the message board regularly if you are expecting a message. Messages cannot be delivered personally.

Catering

Special Dietary Requirements - Please advise the Conference Secretariat, if you have not already done so, of any special dietary requirements.

Accommodation

Accommodation Deposits: All pre-paid accommodation deposits have been credited to your hotel accounts. You are required to pay the balance of your account, plus any incidentals, upon departure. If a credit card number was supplied to guarantee your room, this is being used as a guarantee only (unless requested otherwise) and the full account will need to be settled upon departure.

Parking

Parking at Crowne Plaza Coogee is included for delegates staying at the Crowne Plaza Hotel. The cost for delegates not staying at the hotel is \$4 per hour or a maximum of \$18 per day. Please note that parking for delegates not staying at the hotel is subject to availability and an early arrival is recommended.

Conference Secretariat

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Disclaimer

The views expressed by presenters at this conference are not necessarily those of the RACI Colloid and Surface Science Division. Neither the organising committee nor the Division take responsibility for the content of the presentations or the abstracts that appear in this booklet.

Program

OVERVIEW

Sunday 4 th	15:00 – 17:00	Registration	(Level One, Crowne Plaza Hotel)
	17:00 – 19:00	Welcome Reception	(Pool Terrace, Crowne Plaza Hotel)
		Oceanic Ballroom West	Oceanic Ballroom East
Monday 5 th	08:30		Welcome
	08:50 – 17:30	Spectroscopy and Scattering in Surface & Colloid Science	Surface Forces, Nanotribology and Biological Interactions
	18:00 – 20:00	Poster session and drinks	
Tuesday 6 th	08:00 – 09:40	Inorganic Oxide Surfaces	Surface Forces, Nanotribology and Biological Interactions
	10:10 – 16:20	Inorganic Oxide Surfaces	Drops and Bubbles
	16:20 – dark	Beach time	
Wednesday 7 th	08:30 – 10:30	Plenary Lectures	
	11:00 – 17:30	Hierarchical Materials	Frontiers of Colloid and Interface Science
	17:30	RACI Colloid and Surface Science Division meeting All welcome	
	19:30 – late	Conference Dinner	
Thursday 8 th	09:00 – 14:40	Pharmaceutical Applications	Frontiers of Colloid and Interface Science
	14:40 – 15:00		Closing remarks

Monday 5 February **OCEANIC BALLROOM WEST**

08:30 WELCOME AND OPENING REMARKS (Ballroom East)

SPECTROSCOPY AND SCATTERING IN SURFACE AND COLLOID SCIENCE

Session Chair: Jim McQuillan

Abstract on page

08:50	Keynote: Donald Sparks	The role of X-ray absorption spectroscopy (XAS) in advancing the frontiers of environmental interfacial chemistry	29
09:10		Sparks keynote talk continues.	
09:30	S. Harmer	SRXPS evidence for surface stabilization of transition metal chalcogenide fracture surfaces	30
09:50	D. Beattie	Synchrotron XPS studies of collector co-adsorption on gold and gold:silver alloy surfaces	31
10:10	M. Ree	Synchrotron X-Ray scattering analysis on structures of multi-armed star-shape polystyrenes in solutions	32

10:30 **DRINKS BREAK**

Session Chair: Sarah Harmer

11:00	M. James	What to do when your reactor goes critical	33
11:20	J. Penfold	Interplay between surface and solution behaviour in di-alkyl chain cationic / nonionic surfactant mixtures	34
11:40	J. Santos	Time-resolved optical waveguide spectroscopy for studying protein adsorption kinetics	35
12:00	W. Hamilton	Topological relaxation of shear-induced lamellar phases to sponge phase equilibrium and the energetics of membrane fusion	36
12:20	D. McGillivray	Structure of functional toxin pores in tethered bilayers: membrane association of α -hemolysin	37

12:40 **LUNCH**

Session Chair: David Beattie

13:40	Keynote: Zhan Chen	Molecular structures of polymers and biological molecules at interfaces	38
14:00		Chen keynote talk continues.	
14:20	W. Ducker	A nanoscale gas state	39
14:40	A. Young	In situ IR studies of thiol ligand adsorption on CdS films	40
15:00	J. McQuillan	Probing the cation change capacity and biomineralisation propensity of bacterial surfaces with in situ IR spectroscopy	41

15:20 **DRINKS BREAK**

Session Chair: William Ducker

15:50	P. Mulvaney	The surface chemistry of single nanocrystals	42
16:10	N. Paris	Organic synthesis of fluorinated molecules on GaAs(100) and Cu(100)	43
16:30	A. Nelson	The competitive swelling kinetics of thin polystyrene films by toluene	44
16:50	S. Javadian	Determination of the physico-chemical parameters and aggregation number of surfactant in micelles in binary alcohol-water mixtures	45
17:10	P. Sehgal	Mixed monolayer and micelle formation of cationic and zwitterionic surfactant of identical hydrocarbon tail in an aqueous medium: interfacial tension, fluorescence probe, dynamic light scattering and viscosity study	46

17:30 Talks end

18:00 – 20:00 **POSTER SESSION**

Monday 5 February **OCEANIC BALLROOM EAST**

08:30 WELCOME AND OPENING REMARKS

SURFACE FORCES, NANOTRIBOLOGY AND BIOLOGICAL INTERACTIONS

		<i>Session Chair: Michelle Gee</i>	Abstract on page
08:50	Keynote: Jacob Israelachvili	Frictional properties of confined nanoparticles: effects of particle size and shape	47
09:10		Israelachvili keynote talk continues.	
09:30	S. Ohnishi	The influence of cyclohexane vapor on stick-slip friction between mica surfaces	48
09:50	T. Anderson	Interactions between supported phospholipid bilayers and silica surfaces	49
10:10	K. Higashitani	Nano-tribology of clean hydrophilic silica surfaces in electrolyte solutions of normal and high pH's	50
10:30	DRINKS BREAK		
		<i>Session Chair: Karin Jacobs</i>	
11:00	V. Yaminski	Evaporation-stabilized foam films of pure liquids	51
11:20	A. Luzar	Electrowetting in a nanopore	52
11:40	N. Maeda	Dynamics of capillary-held liquids	53
12:00	T. Becker	Force spectroscopy with AFM: surface charge of specific barite crystal faces	54
12:20	G. Willmott	Effects of surface forces on a torsional ultrasonic oscillator	55
12:40	LUNCH		
		<i>Session Chair: Alenka Luzar</i>	
13:40	D. Bratko	Modeling ion-specific colloidal and protein interactions	56
14:00	Q. Li	Particle-particle and particle-substrate interactions in colloidal self-assembly	57
14:20	M. Clauzel	Forced desorption of surfactant at polymer–water interface	58
14:40	W. Briscoe	Direct measurement of interactions between surface-grown polymer brushes in aqueous media	59
15:00	L. Piculell	Bridging or depletion – is that all there is? “New” mechanisms of destabilisation of aqueous polymer-particle mixtures	60
15:20	DRINKS BREAK		
		<i>Session Chair: Wuge Briscoe</i>	
15:50	M. Mizukami	Liquid structuring induced by solid surface: hydrogen-bonded surface molecular macrocluster	61
16:10	M. Kohonen	Instabilities in the interaction of surfaces coated with thin liquid films	62
16:30	S. Edwards	Patchy surfactant coatings and long-range forces	63
16:50	E. Meyer	Progress in understanding hydrophobic interactions	64
17:10	I. Vakarelski	Anomalous behavior in aqueous thin liquid films in contact with fluorinated materials	65
17:30		Talks end	
18:00 – 20:00	POSTER SESSION		

POSTERS

Monday 5 February 6 – 8 pm, Oceanic Ballroom and Foyer

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SS-1	C. Barton	Mixed monolayers of NTA disulfide and TEG thiol on gold nanoparticle surfaces studied with optical spectroscopy and zeta potential	153
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SS-5	M. James	Characterisation of alkyl-functionalised Si(111) using reflectometry and AC impedance spectroscopy	157
SS-6	C. Pascual-Izarra	Positron annihilation lifetime spectroscopy and small angle X-ray scattering of self-assembled amphiphiles	158
SS-7	J. Penfold	Manipulation of surface adsorption using polyelectrolyte / surfactant mixtures	159
SS-8	L. Petrone	<i>In situ</i> infrared spectroscopic analysis of adhesion processes of small marine organisms	160
SS-9	M. Ree	Small-angle X-ray scattering studies on structure of an enzyme protein in solution	161
SS-10	I. Sedeva	Influence of a polymer depressant on the wettability of model surfaces	162
SS-11	R. Seemann	Networks of liquid bridges in wet granular systems	163
SS-12	P. Sehgal	Interaction and stability of binary mixtures of cationic and nonionic surfactants: interfacial tension and fluorescence probe studies	164
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SURFACE FORCES, NANOTRIBOLOGY and BIOLOGICAL INTERACTIONS			
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SF-6	M. James	The structure of synthetic tropoelastin surfaces	171
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POSTERS Monday 6 – 8 pm ... Oceanic Ballroom and Foyer

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SF-10	I. Vakarelski	Nanoparticles and nanotubes modified scanning probe microscopy tips	175

INORGANIC OXIDE SURFACES

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POSTERS

DROPS and BUBBLES

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POSTERS Monday 6 – 8 pm ... Oceanic Ballroom and Foyer

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HM-6	F. Lie	Assembly of nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$	199
HM-7	B. Nuthakki	Protic ionic liquids and their potential applications	200
HM-8	A. Polyzos	Development of a polyvalent inhibitor of cholera toxin using a bio-functionalised surfactant mesophase	201
HM-9	S. Sagnella	Nonionic amide and monoethanolamide surfactants with isoprenoid-type hydrocarbon chains: thermotropic and lyotropic liquid crystalline phase behaviour	202
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FRONTIERS of COLLOID and INTERFACE SCIENCE

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FR-6	T. Joshi	Mixed systems of cationic – nonionic surfactant systems in water	211
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FR-10	Y.-G. Lee	A novel method for highly monodisperse micron-sized silica particles in room temperature	215
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POSTERS Monday 6 – 8 pm ... Oceanic Ballroom and Foyer

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FR-19	S. Takashina	Effect of the peculiarity of water pool pH of w/o microemulsion on particle synthesis	224
FR-20	H.P. Yap	Colloidal surface engineering: a nanoblended approach	225

PHARMACEUTICAL APPLICATIONS

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PA-7	S.-H. Park	Preparation and membrane fluidity of noble metal nanoparticles loaded DPPC liposomes	232
PA-8	C. Petcu	Magnetic polymer nanoparticles for MRI contrast enhancement	233
PA-9	B. Roberts	Properties of novel non-viral DNA transfection agents	234
PA-10	Dallas Warren	Molecular Dynamics Simulations Of Lipid Formulations With Drug Molecules	235

INORGANIC OXIDE SURFACES

Session Chair: George Franks

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08:00	Keynote: Gordon E. Brown Jr.	Factors controlling the reactivity of metal oxide surfaces	70
08:20		Brown keynote talk continues.	
08:40	S. Sjöberg	Chemical speciation, solubilities and surface complexation in Al(hydr)oxide systems	71
09:00	B. Bickmore	Toward an improved MUSIC model	72
09:20	Y. Gan	Charging behaviour of gibbsite basal (001) surface in NaCl solution investigated by AFM colloidal probe technique	73
09:40	DRINKS BREAK		
		<i>Session Chair: Jonas Addai-Mensah</i>	
10:10	J. Halloran	Freeze casting colloidal suspensions	74
10:30	L. Zou	Using titania/silica and titania/activated carbon photocatalysts to degrade organic pollutants and their regeneration	75
10:50	L. Bergström	Synthesis and assembly of iron oxide nanocrystals	76
11:10	K. N. Pham	Surface charge modification of nano-sized silica colloids	77
11:30	Y.-L. Liu	Surface modification on silicons through silicon-oxide reactions	78
11:50	LUNCH		
		<i>Session Chair: Fred Lange</i>	
12:40	Keynote: Kwadwo Osseo-Asare	Metal oxides in aqueous processing systems: colloids, solutions, and surfaces	79
13:00		Osseo-Asare keynote talk continues.	
13:20	A. Costine	Bayer process scale formation	80
13:40	J. Addai-Mensah	Fundamental studies of aluminium tri-hydroxide crystallization from synthetic supersaturated caustic aluminate liquors	81
14:00	M. Cran	Influence of dispersant architecture upon mineral oxide adsorption	82
14:20	DRINKS BREAK		
		<i>Session Chair: Yang Gan</i>	
14:40	W. Sigmund	Electrospinning of ceramic oxide nanofibers	83
15:00	M. Hill	The single source chemical vapour deposition of inorganic oxide thin film surfaces	84
15:20	F. Lange	Role of specifically adsorbed ions in the lateral epitaxial overgrowth of n-type ZnO in water at 90°C	85
15:40	A. Mierczynska-Vasilev	Tapping mode AFM studies of polymer adsorption on talc and clinocllore	86
16:00	G. Franks	The isoelectric points of basal plane sapphire and alpha alumina powder	87
16:20	BEACH TIME		

SURFACE FORCES, NANOTRIBOLOGY AND BIOLOGICAL INTERACTIONS (Cont.)

		<i>Session Chair: Roger Horn</i>	Abstract on page
08:00	Keynote: Suzanne Giasson	Static and dynamic interactions at biomaterial surfaces	66
08:20		Giasson keynote talk continues	
08:40	K. Vasilev	Effects of charge and ionic strength on the adsorption of lipids onto protein-resistant PEG graft layers	67
09:00	K. Jacobs	Impact of short- and long-range forces on protein conformation and adsorption kinetics	68
09:20	G. Liu	A new electrode interface comprising molecular wires and poly(ethylene glycol) spacer units for probing protein electrochemistry	69
09:40	DRINKS BREAK		
	DROPS AND BUBBLES		
		<i>Session Chair: Ray Dagastine</i>	
10:10	Keynote: Darsh Wasan	Foams and emulsions: thin liquid film approach	88
10:30		Wasan keynote talk continues	
10:50	P. Spicer	Dewetting and crystallization in emulsion droplets: colloid synthesis and purification	89
11:10	T. Wooster	Interfacial structure and emulsion stability of protein-carbohydrate di-block copolymers	90
11:30	J. Beattie	Water at hydrophobic interfaces	91
11:50	LUNCH		
		<i>Session Chair: Clive Prestidge</i>	
12:40	Keynote: Eric Furst	Direct measurements of colloidal interactions at the oil-water interface	92
13:00		Furst keynote talk continues.	
13:20	L. Gauckler	Foams derived from particle suspensions	93
13:40	E. Herzig	Bicontinuous emulsions stabilised with silica particles	94
14:00	R. Pugh	Silica nanoparticles: surface characterisation and foaming	95
14:20	DRINKS BREAK		
		<i>Session Chair: Grant Webber</i>	
14:40	R. Dagastine	Dynamic forces in emulsions measured with AFM	96
15:00	D. Chan	A general theoretical perspective of dynamical interactions involving drops and bubbles	97
15:20	N. Jain	Determination of forces between emulsion drops in water-in-oil emulsion by neutron scattering and optical interferometry	98
15:40	M. Krasowska	Effect of hydrophobicity and surface charge on wetting and time-scale of attachment of bubbles to solids	99
16:00	V. Craig	Specific ion effects on bubble coalescence inhibition in mixed electrolyte systems	100
16:20	BEACH TIME		

Wednesday 7 February **OCEANIC BALLROOM WEST**

08:30	RACI Colloid & Surface Science Division Plenary Lecture: Prof. Wolfgang Knoll	101
	“Supramolecular interfacial architectures for optical biosensing”	
	<i>Chair: Dr. Patrick Hartley</i>	
09:30	A.E. Alexander Lecture: Prof. Brian Vincent,	102
	“Microgel particles: an overview”	
	<i>Chair: A/Prof. Bob Hunter</i>	
10:30	DRINKS BREAK	
	HIERARCHICAL MATERIALS	
	<i>Session Chair: Calum Drummond</i>	Abstract on page
11:00	Keynote: Eric Amis	High throughput approaches to polymer formulation 103
11:20		Amis keynote talk continues.
11:40	G. Warr	In situ polymerization and self-assembly of cationic surfactants 104
12:00	M. Lu	Proton conductive composite membrane of phosphosilicate and polyvinyl alcohol 105
12:20	N. Ishida	Structural behaviour of thermoresponsive polymer-grafted surface in aqueous solutions 106
12:40	LUNCH	
	<i>Session Chair: Eric Amis</i>	
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14:00	V. Milam	Reversible DNA linkages in model, multiparticle therapeutic assemblies 108
14:20	C. Conn	Dynamics of structural transformations between lamellar and inverse bicontinuous cubic lyotropic mesophases 109
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Wednesday 7 February **OCEANIC BALLROOM EAST**

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 “Supramolecular interfacial architectures for optical biosensing”
Chair: Dr. Patrick Hartley

09:30 **A.E. Alexander Lecture: Prof. Brian Vincent** 102
 “Microgel particles: an overview”
Chair: A/Prof. Bob Hunter

10:30 **DRINKS BREAK**

FRONTIERS OF COLLOID AND INTERFACE SCIENCE

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11:20 Eastoe keynote talk continues.

11:40 S. Notley Surface interactions with biomacromolecular surfaces derived from wood 117

12:00 Q. Li Pattern formation on tilted substrates by colloidal self-assembly using flow-controlled vertical deposition method 118

12:20 S. Hyde Polyphile and mikto-arm self-assembly: possible mesostructures 119

12:40 **LUNCH**

Session Chair: Julian Eastoe

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14:00 R. Atkin Phase behaviour and microstructure of microemulsions with a room temperature ionic liquid as the polar phase 121

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Sponsored by Scientific Solutions

PHARMACEUTICAL APPLICATIONS

Session Chair: Ben Boyd

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Session Chair: Ian Larson

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14:20	F. Caruso	Bridging the materials and life science divide: bioinspired colloidal systems	141
14:40	CLOSING REMARKS		
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Plenary and Keynote Speakers



Prof. Wolfgang Knoll

Max-Planck Institute for Polymer Research
Mainz, Germany

Plenary Lecturer

Sponsored by the Royal Australian Chemical
Institute, Colloid and Surface Science Division.

Wolfgang's lecture "Supramolecular interfacial architectures for optical biosensing" will be in the plenary session at 8:30 on Wednesday morning. His abstract can be found on p. 101.

Prof. Dr. Wolfgang Knoll joined the Max Planck Society in 1993 as one of the directors at the MPI for Polymer Research. After a physics education at the Technical University of Karlsruhe, he received a PhD degree in biophysics at the University of Konstanz in 1976. In 1977 he joined the group of Prof. E. Sackmann at the University of Ulm working on model membrane systems and their phase behavior by neutron scattering, spectroscopic and thermodynamic measurements. After a post-doctoral stay at the IBM Research Laboratory in San Jose, California, (1980/ 1981) and a stay as a visiting scientist at the Institute Laue-Langevin in Grenoble he followed Prof. Sackmann to the Physics Dept. of the TU of Munich. There, he continued research on various aspects of the structure, order, and dynamics of lipid membranes. He also started work on evanescent wave optics for the characterization of interfaces and ultrathin coatings. Following another visiting scientist appointment at the IBM Research Laboratory in San Jose, he received the Habilitation from the TU Munich in 1986. After a short period as a Heisenberg fellow he was offered the same year a position at the Associate Professor level at the MPI for Polymer Research in the group of Prof. Spiess, with a joint appointment as Privatdozent at the University of Mainz in 1987. In 1990 he received the Heinrich Welker Award and was teaching at the University of Erlangen-Nürnberg. From 1991 to 1999 he was Head of Laboratory for Exotic Nanomaterials hosted by the Institute of Physical and Chemical Research (RIKEN) in Wako, Japan. In 1992, he was appointed Consulting Professor at the Dept. of Chemical Engineering at Stanford University, California, where he participates in the NSF-funded Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA) with a small group working on bio-interfaces. In 1998 he was appointed Professor of Chemistry (by Courtesy) at the University of Florida in Gainesville, and in 1999 Adjunct Professor at Hanyang University in Seoul, Korea. Since 1999 he is also a Temasek Professor at the National University of Singapore, directing a research group on Functional Materials and Bio-Interfaces. He is the 2003 recipient of the Eugen-and-Inge- Seibold-Award.

His current research interests include aspects of the structure/ order - property/ function relationships of polymeric/ organic systems, in particular, in thin films and at functionalized surfaces. Strong emphasis is put on optical techniques to elucidate the structural and functional properties of supramolecular assemblies and nano-materials.



Prof. Brian Vincent
University of Bristol, UK

A.E. Alexander Lecturer

Sponsored by the University of Sydney.

Brian's lecture "Microgel particles: an overview" will be in the plenary session at 9:30 on Wednesday morning. See his abstract on p. 102.

Professor Vincent leads the Polymer and Colloid Group at Bristol University. He has strong research interests in a wide variety of areas, looking at systems of both academic and industrial significance. Research topics include microgel particles, monodisperse and surfactant-free "silicone" oil-in-water emulsions; a variety of core-shell systems, microemulsions, adsorption studies of polymers and their influence on dispersancy properties; and particle deposition/adsorption onto macroscopic surfaces.

Professor Vincent's current interests and roles include: Leverhulme Professor of Physical Chemistry, University of Bristol (since 1992); Head of the Academic Colloid Group at the University of Bristol; Director of the Bristol Colloid Centre; Immediate Past President of the International Association of Colloid and Interface Scientists (IACIS); Chairman of The Colloid and Interface Science Group of the Faraday Division of The Royal Society of Chemistry; Member of Faraday Division Council; Member of the Polymer Colloids Forum; Chair of the Technical Advisory Board of the Ian Wark Research Institute, University of South Australia.

The A.E. Alexander Lecture was established in 1978 as a result of an appeal by the University of Sydney and the RACI Division of Colloid and Surface Chemistry to commemorate Professor Albert "Alex" Alexander FAA FRACI, who was Professor of Physical Chemistry at the University of Sydney from 1957-1970. The Alexander Lecturer is an eminent scientist who has contributed particularly to Colloid and Surface Science in Australia.

Prof. Donald L. Sparks
University of Delaware, USA

**Keynote Speaker in the theme Spectroscopy
and Scattering in Surface and Colloid Science**

Sponsored by the Australian Synchrotron.

Donald's lecture "The role of X-ray absorption spectroscopy in advancing the frontiers of environmental interfacial chemistry" is scheduled for Monday at 8:50 am, in the West ballroom. See his abstract on p.29.



Donald L. Sparks is the S. Hallock du Pont Endowed Chair at the University of Delaware. He is internationally recognized for his research in the areas of kinetics of geochemical processes and mechanisms of metal/oxyanion/nutrient reactions at biogeochemical interfaces using in-situ spectroscopic and microscopic techniques. He is the author or coauthor of 270 publications including two widely adopted textbooks, *Kinetics of Soil Chemical Processes and Environmental Soil Chemistry (two editions)*. Dr. Sparks has given plenary and keynote presentations throughout the world and he has mentored more than 70 graduate students and postdoctoral fellows.



A/Prof. Zhan Chen
University of Michigan, USA

**Keynote Speaker in the theme Spectroscopy
and Scattering in Surface and Colloid Science**

Sponsored by Lastek.

Zhan's lecture "The role of X-ray absorption spectroscopy in advancing the frontiers of environmental interfacial chemistry" is scheduled for Monday at 1:40 pm, in the West ballroom. See his abstract on p. 38.

Zhan Chen received his PhD degree in Chemistry from the University of California at Berkeley. He did his postdoctoral research at the Lawrence Berkeley National Laboratory. Currently he is an associate professor in the Department of Chemistry at the University of Michigan. He also holds joint appointments in Department of Macromolecular Science and Engineering, Applied Physics Program, Biophysics, and Optical Physics Interdisciplinary Laboratory at the University of Michigan. His research is focused on the elucidation of molecular structures of polymers and biological molecules at interfaces using various spectroscopic techniques.

Prof. Jacob N. Israelachvili

University of California Santa Barbara, USA

**Keynote Speaker in the theme Surface Forces,
Nanotribology and Biological Interactions**

Sponsored by the Particulate Fluids Processing
Centre, University of Melbourne.

*Jacob's lecture "Frictional properties of confined
nanoparticles: effects of particle size and shape" is
scheduled for Monday at 8:50 am, in the East
ballroom. See his abstract on p. 47.*



Jacob Israelachvili received his BA and MA in Physics from the University of Cambridge, England, and also carried out graduate and postgraduate research work there at the Surface Physics Department of the Cavendish Laboratory. He received his PhD in 1972. After a two-year European Molecular Biology Organization (EMBO) research fellowship at the University of Stockholm, he left for Australia where, from 1974 to 1986, he led an experimental research laboratory devoted to measuring forces between surfaces. In 1982 he was elected a member of the Australian Academy of Science. In 1986 he joined the faculty of the University of California at Santa Barbara where he holds joint appointments as Professor in the Department of Chemical Engineering, the Materials Department and the Biomolecular Science and Engineering Department. He was the Associate Director of the Materials Research Laboratory at UCSB from 1993 until 2003. In 1988 he was elected a Fellow of the Royal Society of London, and in 1991 he was awarded the Alpha Chi Sigma Award for Chemical Engineering Research by the American Institute of Chemical Engineers. In 1996 he was elected a Foreign Associate of the US National Academy of Engineering. He is the author of a textbook entitled "Intermolecular and Surface Forces" (Academic Press, 2nd Edition: 1991). He was given the 2002-03 Adhesion Society's Award for Excellence in Adhesion Science, sponsored by 3M. Most recently he was made a Fellow of the American Physical Society (2003) and was elected a member of the National Academy of Sciences in 2004.



A/Prof. Suzanne Giasson

Université de Montréal, Canada

**Keynote Speaker in the theme Surface Forces,
Nanotribology and Biological Interactions**

Sponsored by Ian Wark Research Institute,
University of South Australia.

*Suzanne's lecture "Static and dynamic
interactions at biomaterial surfaces" is scheduled
for Tuesday at 8:00 am, in the East ballroom. See
her abstract on p. 66.*

Dr. Suzanne Giasson, is currently Associate Professor in the Department of Chemistry and Faculty of Pharmacy, University of Montreal, since 2002, prior to which she held a faculty

position in the department of Chemical Engineering at University Laval, Québec, Canada, for 6 years. She received her Ph.D in Chemical Engineering from the Université Pierre & Marie Curie in Paris, France and the University of Western Ontario in London, Canada, in 1992.

Her research focuses on understanding and utilizing the special properties of macromolecules (polymers and biomolecules) at solid/aqueous interfaces to develop surface modification processes and smart materials exhibiting reversible and tuneable properties. Her approach consists to correlate surface properties of macromolecules (degree of ionization, effective charge, molecular structure, surface grafting density, etc) and their behaviour (structural changes, adhesion, shear response, etc) under different environmental conditions (ionic strengths, pH, compression, shear). Various techniques including Surface Forces Apparatus, AFM, ellipsometry, X-ray reflectometry, Langmuir balance and simulations are used.



Prof. Kwadwo Osseo-Asare
Pennsylvania State University, USA

Keynote Speaker in the theme Inorganic Oxide Surfaces

Sponsored by the Ian Potter Foundation.

Kwadwo's lecture "Metal oxides in aqueous processing systems: colloids, solutions, and surfaces" is scheduled for Tuesday at 12:40 pm, in the West ballroom. See his abstract on p. 79.

Kwadwo Osseo-Asare is Distinguished Professor of Metallurgy and Energy and Geo-environmental Engineering in the Department of Materials Science and Engineering at Penn State University.

He received his B.S., M.S. and Ph.D. in Materials Science and Engineering from the University of California (Berkeley) in 1970, 1972 and 1975, respectively. He joined the faculty at Penn State in 1976 where he was promoted to professor in 1984 and served as chair of the Metals Science and Engineering Program from 1995-2000. He has published over 200 papers and supervised nearly forty M.S. and Ph.D. theses. He was elected a member of the National Academy of Engineering in 2004 for contributions to the fundamental understanding of interfacial phenomena in leaching and solvent extraction. His research interests include aqueous processing: hydrometallurgy, separation science & technology, environmental systems, materials synthesis & processing, wet processing in semiconductor fabrication, surface cleaning & finishing. applied aqueous chemistry: interfacial and colloidal phenomena, surfactant science, semiconductor electrochemistry, and thermodynamic modeling.

Prof. Gordon E. Brown, Jr.
Stanford University, USA

Keynote Speaker in the theme Inorganic Oxide Surfaces

Sponsored by the Particulate Fluids Processing Centre, University of Melbourne.

Gordon's lecture "Factors controlling the reactivity of metal oxide surfaces" will be on Tuesday at 8:00 am, in the West ballroom. His abstract can be found on p. 70.



Gordon Brown is the Dorrell William Kirby Professor at Stanford University, School of Earth Sciences. He received his PhD in 1970 in Mineralogy and Crystallography at Virginia Polytechnic Institute and State University. Since 2004 he has been Director, Stanford Environmental Molecular Science Institute at Stanford University; since 1998, Chair, Stanford Synchrotron Radiation Laboratory Faculty; since 1992, Professor, Stanford Synchrotron Radiation Laboratory Faculty; since 1986, Professor of Mineralogy and Geochemistry at Stanford University. In 2000 he was elected a Fellow of the American Association for the Advancement of Science. His research focuses on surface and interface geochemistry; environmental fate of heavy metals and applications of synchrotron radiation in geochemistry and mineralogy.



Prof. Darsh Wasan
Illinois Institute of Technology, USA

Keynote Speaker in the theme Drops and Bubbles

Darsh's lecture "Foams, emulsions and dispersions" is scheduled for Tuesday at 10:10 am, in the East ballroom. His abstract can be found on p. 88.

Darsh Wasan holds a B.S. degree from the University of Illinois at Urbana-Champaign and a Ph.D. from the University of California at Berkeley, both in Chemical Engineering. He has spent his entire professional career at IIT, beginning in 1964, and is currently Motorola Chair Professor of Chemical Engineering and Vice President. He has held virtually every academic and administrative post, including department chairman, dean of engineering, vice president for research and technology and vice president for academic affairs and provost. He has over 380 publications, and is a co-author of a textbook (with Edwards and Brenner) on *Interfacial Transport Processes and Rheology*. He has supervised and mentored 55 Ph.D. and 60 M.S. students, and 15 postdoctoral fellows. He received the American Chemical Society National

Award in Colloid and Surface Chemistry in 2000, and the Langmuir Lectureship Award in 2004; the American Institute of Chemical Engineers Award in Fluid-Particle Systems in 2002, and the Alpha Chi Sigma Award for Fundamental and Applied Chemical Engineering Research in 2005. He received the National Science Foundation's Special Creativity Award twice. He has received the excellence in teaching awards from both IIT and the American Society for Engineering Education. He was elected to the U.S. National Academy of Engineering in 2004 and to the Indian National Academy of Engineering in 2006. He is editor-in-chief of the *Journal of Colloid and Interface Science*.

Prof. Eric M. Furst

University of Delaware, USA

Keynote Speaker in the Drops & Bubbles theme

Sponsored by Orica Mining Services.

Eric's lecture "Direct measurement of colloidal interactions at the oil-water interface" is on Tuesday at 12:40 pm, in the East ballroom. His abstract is on p. 92.



Eric M. Furst received his Bachelors degree in Chemical Engineering with University Honors from Carnegie Mellon University in 1995, and in 2000, earned his PhD at Stanford University for his work with Prof. Alice Gast on the development of light scattering and optical trapping methods to study colloidal interactions and micromechanics. In 2001, after his postdoctoral work in biophysics at Institut Curie, Paris, Furst joined the Chemical Engineering faculty at the University of Delaware. His current research interests are in complex fluid rheology, directed colloidal assembly, colloidal interactions, microrheology and the biophysics of cell-material interactions. Furst is the recent recipient of an NSF CAREER Award and a DuPont Young Investigator Award.



Prof. Eric Amis

National Institute of Standards and Technology, USA

Keynote Speaker in the theme Hierarchical Materials

Eric's lecture "High throughput approaches to polymer formulation" is scheduled for Wednesday at 11:00 am, in the West ballroom. His abstract can be found on p. 103.

Dr. Eric J. Amis is the Deputy Director of the Materials Science and Engineering Laboratory of the National Institute of Standards and Technology. Before he joined NIST, Dr. Amis spent

11 years on the faculty in chemistry at the University of Southern California. His research interests are application of rheology with light, neutron and X ray scattering to investigate the physics of complex soft materials. More recently, he initiated the novel application of combinatorial and high throughput methods for investigations of materials science, which led to the establishment of the NIST Combinatorial Methods Center and an innovative program in measurement methods for systematic investigations of biomaterial interactions. He has over 140 peer-reviewed publications.

Prof. Ulrich Schubert

Technical University of Eindhoven, The Netherlands



Keynote Speaker in the theme Hierarchical Materials

Ulrich S. Schubert was born in Tübingen in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth (both Germany) and the Virginia Commonwealth University, Richmond (USA). His Ph.D. work was performed under the supervision of Professor Eisenbach (Bayreuth, Germany) and Professor Newkome (Florida, USA). In 1995 he obtained his doctorate with Prof. Eisenbach. After a postdoctoral training with Professor Lehn at the Université Strasbourg (France) he moved to the Technische Universität München (Germany) to obtain his habilitation in 1999 (with Professor Nuyken). From 1999 to spring 2000 he held a temporary position as a professor at the Center for NanoScience at the Technische Universität München (Germany). Since Summer 2000 he has been Full-Professor at the Eindhoven University of Technology. His Awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Fachgruppe Makromolekulare Chemie), the Heisenberg-Stipendium of the DFG, the Dozenten-Stipendium of the Fonds der Chemische Industrie and the VICI award of NWO. The major focus of the research interest of his relates to heterocyclic chemistry, supramolecular materials, surface chemistry, nanoscience and tailor-made macromolecules.



Prof. Julian Eastoe

University of Bristol, UK

Keynote Speaker in the theme Frontiers of Colloid and Interface Science

Sponsored by ANSTO

Julian's lecture "Rêves moléculaires en oxygène et carbone" will be given at 11:00 am on Wednesday, in the East ballroom. His abstract can be found on p. 116.

Julian Eastoe has been a full faculty member of the School of Chemistry, University of Bristol, UK, since 1993, prior to which he held the positions of lecturer at the University of Durham and physicist at the Institut Max-von-Laue Paul Langevin in Grenoble, France. He was awarded a Ph.D. in chemistry by the University of East Anglia in 1990.

Julian's research focuses on surface and interfacial aspects of colloid science involving novel surfactants and polymers. His research group develops new functionalised surfactants employing molecular design, synthesis, NMR, and mass spectroscopy techniques. Tensiometric methods in addition to neutron scattering methods are used to probe interfacial and self assembly properties. This work is described in some 130 peer reviewed publications authored or co-authored by Julian and in over 100 invited talks.



Prof. Robert Pelton
McMaster University, Canada

Keynote Speaker in the theme Frontiers of Colloid and Interface Science

Sponsored by CRC Smartprint

Robert's lecture "Adhesion to wet cellulose – design rules for polymers, peptides and proteins" will be given at 9:00 am on Thursday, in the East ballroom. His abstract can be found on p. 130.

Robert Pelton (Ph.D. 1977, Bristol University UK, Colloid Chemistry) holds a Tier 1 Canada Research Chair in Interfacial Technologies. His 180+ peer reviewed publications include often cited works with PNIPAM (N-isopropylacrylamide) temperature sensitive microgels which Pelton invented in 1978 (published in 1986, ref 19 in publication list). Since then, the McMaster group has established itself as one of the world's most prolific academic group involved in designing new polymers which improve the strength and function of paper-based materials. More recently, they are focusing on inducing bio-functionality into paper-based materials. Dr. Pelton's group is considered the world's largest, most prolific academic research group working in the area of polymers for papermaking. His laboratory provides ideal opportunities for graduate students and postdoctoral fellows to learn how to design, synthesize and characterize polymers, put them into paper materials, and measure and model paper properties, thus providing valuable tools for Canadian papermakers.



Prof. Frank Szoka, Jr.
University of California San Francisco, USA

Keynote Speaker in the Pharmaceutical Applications theme

Sponsored by Starpharma and The Ian Potter Foundation.

Frank's lecture "Dendritic polymers as drug carriers" will be at 9:00 am on Thursday, in the West ballroom. His abstract can be found on p. 142.

Francis C. Szoka is a Professor of Biopharmaceutical Sciences and Pharmaceutical Chemistry at the University of California, San Francisco. He directs a group that devises drug and gene carriers and examines their mechanism of action in cells and animals. His group studies liposomes, peptides and polymers and has described their findings in over 160 manuscripts and 25 US patents. He received his Ph.D. in Biochemistry in 1976 from SUNY/Buffalo. He is the co-founder of Sequus, a liposome drug delivery company that created Doxil™ now owned by Johnson & Johnson and of GeneMedicine, Inc., a gene therapy company, now known as Valentis, Inc.

Dr. Rob Price
University of Bath, UK

Keynote Speaker in the Pharmaceutical Applications theme

Sponsored by the Victorian College of Pharmacy, Monash University

Rob's lecture "Novel engineering of colloidal particles for pharmaceutical systems" will be given at 10:50 am on Thursday, in the West ballroom. His abstract can be found on p. 145.



Dr Robert Price is currently a reader at the Department of Pharmacy and Pharmacology, University of Bath where he founded the Pharmaceutical Surface Science research group. Dr Price has developed expertise in the field of pharmaceutical surface science and particle engineering of colloidal systems. The particular emphasis of his research work is on investigating the physicochemical properties which govern particle adhesion, surface stability issues of processed particles and the general areas of particle technology and crystal growth.

THE ROLE OF X-RAY ABSORPTION SPECTROSCOPY (XAS) IN ADVANCING THE FRONTIERS OF ENVIRONMENTAL INTERFACIAL CHEMISTRY

Donald L. Sparks

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There have been major advances in the development and use of state-of-the-art in-situ synchrotron-based techniques that enable one to study an array of important interfacial reactions and processes at the molecular scale. One of the most widely used techniques is x-ray absorption spectroscopy (XAS). XAS can be used to study most elements in crystalline or non-crystalline solid, liquid, or gaseous states over a concentration range of a few mg/L to the pure element. XAS can be used to probe structural sites ranging from those in crystals and glasses to those at interfaces such as mineral/water and mineral/microbe. With advanced generation synchrotron light sources that provide x-ray energies ranging from the infrared to the hard x-ray region, higher flux and more intense brightness, beamline optics that produce microfocussed beams for spectromicroscopy and imaging studies, and state-of-the-art detectors, important advances in many scientific areas, including surface and colloid science, will occur over the next decade.

One of the major advantages of XAS, particularly if one wants to simulate natural conditions in natural systems, is that one can study reactions in the presence of water (*in situ*). This is a major advantage over many other molecular scale techniques, which are *ex-situ*, often requiring drying of the sample material, placing it in an ultra-high vacuum (UHV), heating the sample or employing particle bombardment. Such conditions can alter the sample, creating artefacts, and do not simulate most natural environmental conditions. It is especially important to study environmental reactions and processes in water as it is the principal medium of transport of inorganic and organic species, and biochemical reactions take place in aqueous media and across biological membranes that are water based. XAS is an element specific, bulk method that yields information about the local structural and compositional environment of an absorbing atom. It “sees” only the 2 or 3 closest shells of neighbors around an absorbing atom due to the short electron mean free path in most substances. Using XAS, one can ascertain important chemical information such as the oxidation state, information about next nearest neighbors, bond distances and coordination numbers.

The use of XAS and other synchrotron- based techniques (x-ray fluorescence spectroscopy, microtomography, and spectromicroscopy) to study reactions and processes in terrestrial and aquatic environments will be highlighted in this presentation. These include: reaction mechanisms of ions at mineral/humic substance/water and mineral/microbe interfaces, functional group distribution and structure of humic substances, and speciation of contaminants in heterogeneous systems such as soils, sediments, and plants.

SRXPS EVIDENCE FOR SURFACE STABILIZATION OF TRANSITION METAL CHALCOGENIDE FRACTURE SURFACES

S.L. Harmer¹, G.U. von Oertzen¹, W.M. Skinner¹, H.W. Nesbitt²

¹Ian Wark Research Institute, AMSRI, University of South Australia, Mawson Lake Campus, Mawson Lakes, Adelaide, South Australia, 5092

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Sulphide ores include some of our most exploited sources of metals such as Cu, Fe, Zn and Ni, consequently, they are of great interest to the mining community. Metal sulphides are commonly extracted from their ores by flotation and the efficiency of their recovery is dominated by their surface properties. The preparation of ores for industrial beneficiation and extraction processes such as flotation and leaching often involves grinding them to specific size fractions. The result is the production of fractured and cleaved surfaces that often have dissimilar properties than the bulk of the material. These surfaces are then commonly exposed to air, water, collectors and frothing agents during flotation procedures. Understanding the surface chemistry of these minerals provides insight into their reactivity and reaction mechanisms, and ultimately opens a route to controlled manipulation of the surface properties of these materials for custom applications in metal extraction.

Metal chalcogenides may fracture by cleavage along crystal directions or, more commonly, conchoidally (poor cleavage). The fracture of the material involves breaking of bonds between surface atoms, resulting in the formation of high energy dangling bonds and reduced co-ordination (and altered symmetry) at the fracture surface. The response (relaxation) of a surface to fracture is dependant on: crystal orientation; electronegativities of the atoms involved; defects; and impurities. The formation of new bonding configurations (reconstruction), in particular, will be constrained by the possible bond geometries at the surface, orbital direction limitations and potentially significant electron density changes (changes in effective oxidation state).

Synchrotron radiation excited X-ray photoelectron spectroscopy (SR-XPS) and conventional XPS have been used to study the insitu fracture surfaces of a series of industrially important transition metal chalcogenides. These studies were complemented by parallel, ab initio, quantum mechanical simulations of bulk and fracture-surface electronic DOS and electron population. The outcomes of these studies provide links between crystal structure, electronic structure and surface speciation resulting from stabilization of fracture surfaces. Predictable and systematic changes in the surface stabilization of chalcogenides have been observed. Electronic structure measurements of the surface and bulk of insitu fractured minerals has provided information on metal chalcogenide bonding, surface states and offers information on potential surface sites for adsorption. Changes in surface speciation as a function of crystal structure, has provided a route for prediction of mineral surface properties and reactivities.

SYNCHROTRON XPS STUDIES OF COLLECTOR CO-ADSORPTION ON GOLD AND GOLD: SILVER ALLOY SURFACES

David A. Beattie, Ivan Kempson, and William Skinner

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In flotation of base metal sulfides, the selective adsorption of surfactants (termed collectors) is often used to impart high levels of hydrophobicity to valuable mineral particles. In copper-gold processing operations, collectors used to optimize for copper sulfide mineral collection do not normally interact strongly with gold surfaces. It is therefore common for flotation circuits to operate with two or more collector reagents in an effort to optimize for both sulfide minerals and gold. Little is known about the co-adsorption or sequential adsorption of these reagents on gold surfaces, or on gold containing significant amounts of silver (i.e. electrum).

In this study, the co-adsorption and sequential adsorption of different collectors (binary combinations of heptyl xanthate, mercaptobenzothiazole, and diamyl dithiophosphate) on gold and gold:silver alloy surfaces has been studied using synchrotron X-ray photoelectron spectroscopy. The use of synchrotron radiation (NSRRC, Taiwan) and a newly designed/built soft X-ray endstation (commissioned in Taiwan and to be installed at the Australian Synchrotron) have enabled the collection of high resolution spectra of the sulphur 2p peak for the adsorbed collectors. All three collectors were observed to adsorb on both gold and gold:silver surfaces. In addition, both surfaces were shown to co-adsorb combinations of the collectors and sequentially adsorbed combinations, irrespective of the order of addition, although with some variation in the relative adsorbed amounts. The impact of the observed adsorption behaviour is discussed in the context of optimising recovery of gold in copper-gold mineral processing operations.

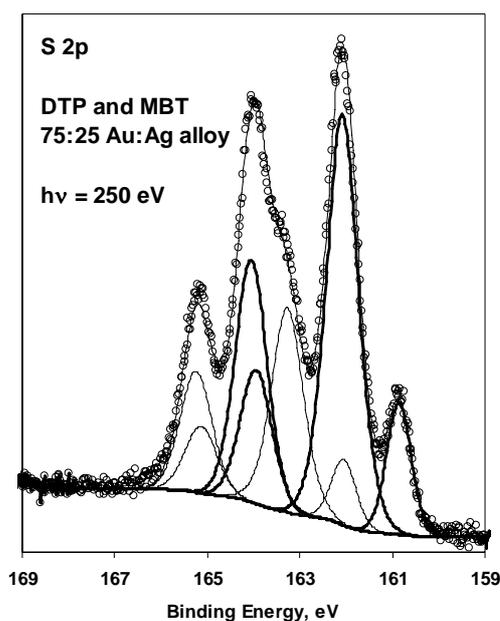


Figure 1 – Synchrotron XPS S 2p spectrum of a 75/25 (atom %) Au/Ag surface after sequential adsorption of diamyl dithiophosphate (DTP) and mercaptobenzothiazole (MBT).

SYNCHROTRON X-RAY SCATTERING ANALYSIS ON STRUCTURES OF MULTI-ARMED STAR-SHAPE POLYSTYRENES IN SOLUTIONS

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Star-shape polymers have gained great attention because of their interesting properties and potential applications. In the present study, a series of star-polystyrenes with 6-57 arms were synthesized. In addition, linear polystyrenes were purchased. Solutions of each polystyrene sample were prepared at a concentration of 1-4 wt% in tetrahydrofuran, a good solvent and cyclohexane at 35°C, a theta solvent. Small-angle X-ray scattering (SAXS) measurements were conducted at the 4C1 beamline (BL) of the Pohang Accelerator Laboratory. The scattering profiles of the linear polystyrenes were confirmed to reveal the characteristics of a Gaussian coil, which has a Gaussian sphere behaving self-avoiding random walk in the solvent but excluded volume effect in the theta solvent. In comparison, the 6-armed polystyrene reveals scattering profiles varying with a power law of q^{-2} in the Debye region, and the 57-armed polystyrene exhibits scattering profiles following a power law of q^{-4} in the Debye region regardless of the good solvent and theta solvent. The other armed polystyrenes show scattering profiles which follow an intermediate power law between those observed for the 6- and 57-armed polystyrenes over the Debye region. All the structural details, which were extracted from the SAXS profiles, will be discussed with considering the chemical nature of the inner and outer parts in the multi-armed polystyrene and the number of arms.

This study was supported by the Korea Science & Engineering Foundation (Korea-Japan Basic Science Cooperation Program and National Research Lab Program) and by the Ministry of Education (BK21 Program). Synchrotron GIXS measurements at the Pohang Accelerator Laboratory were supported by the Ministry of Science & Technology and the POSCO.

WHAT TO DO WHEN YOUR REACTOR GOES CRITICAL

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Soft condensed matter research in Australia using neutron and X-ray scattering is about to enter a “golden age”, with the startup of bright new neutron and photon sources in Sydney and Melbourne respectively. The OPAL Research Reactor and the Australian Synchrotron together represent an investment well in excess of \$500M, and together can be considered as the greatest single investment in scientific infrastructure in Australia’s history. They will essentially be “sister” facilities, with a common open user ethos, and a vision to play a major role in international science.

This presentation will concentrate on the OPAL Research Reactor Facility, which will be the first to come on line. The reactor achieved criticality in August 2006 and reached full power (20 MW) two months later. Instrument commissioning experiments started in late 2006 and it is planned that the formal user program will have commenced by mid-2007. Seven of the first nine instruments will become available in 2007 for routine operation. The majority will be specifically targeted for material science, engineering, physics and crystallography; however, two truly world-class instruments will drive soft condensed matter research at this facility. The *Platypus* neutron reflectometer will enable study of nanoscale thin-films and interfaces; while the *Quokka* Small Angle Neutron Scattering instrument has been built for investigations of bulk nanoscale systems. Partnered with an X-ray reflectometer and a Small Angle X-ray Scattering instrument only metres away from their neutron big brothers, our scientific performance will be competitive with the best research-reactor facilities anywhere.

In my presentation I will give an update on the status of the OPAL facility, examples of its scientific potential, and also show some of the first data to come off the *Platypus* and *Quokka* neutron scattering instruments.

INTERPLAY BETWEEN SURFACE AND SOLUTION BEHAVIOUR IN DI-ALKYL CHAIN CATIONIC / NONIONIC SURFACTANT MIXTURES.

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Understanding the complex surface and solution behaviour of di-alkyl chain cationic and nonionic surfactant mixtures is important for a wide range of applications, which include detergents, shampoos, and conditioners. Furthermore, by analogy, it has wider implications for membrane solubilisation, a key technique in biochemistry, and for the manipulation of membrane properties.

Neutron reflectivity, small angle neutron scattering, light scattering, and surface tension have been used to characterize the surface and solution behaviour of the di-alkyl chain cationic surfactant, di-hexadecyl dimethyl ammonium bromide, DHDAB, with a range of different nonionic surfactants, from C₁₂E₃ to C₁₂E₁₂.

The solution phase behaviour for the different cationic / nonionic mixtures has been determined in some detail. For the nonionic surfactants C₁₂E₆ and C₁₂E₁₂ the nonionic rich region of the phase diagram is comprised of mixed globular micelles. For the cationic rich composition the predominant microstructures are bi-lamellar to multi-lamellar vesicles and L_β lamellar phase. At intermediate compositions there is a coexistence region comprising of the micellar and planar structures in coexistence. For C₁₂E₃ the phase behaviour is different and shows an evolution of different planar structures with composition.

The surface behaviour is characterized by a marked departure from ideal mixing which is more extreme than is normally encountered in surfactant mixtures. For solutions rich in cationic the surface adsorption is dominated by the cationic surfactant, and the nonionic only competes for the surface for solutions rich in the nonionic surfactant. It is shown how this surface behaviour is correlated with the solution phase behaviour which is determining the relative monomer composition and concentrations.

TIME-RESOLVED OPTICAL WAVEGUIDE SPECTROSCOPY FOR STUDYING PROTEIN ADSORPTION KINETICS

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A time-resolved evanescent wave absorption technique is employed in studying the adsorption of protein molecules from an electrolyte-free solution on a hydrophilic glass surface. The method combines the sensitivity of a fast-scan spectral analyzer and surface specificity of slab optical waveguide (SOWG) technique. While proteins are viewed to undergo an overall irreversible adsorption process brought about by structural changes that occur after the initial adsorption phase, we have used an SOWG technique to investigate the first stage of the adsorption process while no noticeable changes have taken place. Absorbance data within the first two seconds after contact fit well into the reversible adsorption model characteristic of Langmuir-type adsorption but the goodness-of-fit diminishes as the protein molecules spend more time on the surface.

TOPOLOGICAL RELAXATION OF SHEAR-INDUCED LAMELLAR PHASES TO SPONGE PHASE EQUILIBRIUM AND THE ENERGETICS OF MEMBRANE FUSION

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While the fusion of bilayer membranes to create a solution passage is important in surfactant chemistry and crucial in biology, detailed information about the process is difficult to come by – as it also generally occurs as an isolated event against a confusing background of other phenomena or responses. Not that membrane passages or their formation need be rare - in the aptly named “sponge” phases a dynamically shifting network of such connections continuously being created and disrupted literally saturates a solution. Interestingly enough, the adjacent stacked lamellar phase in such systems is essentially passage free. This characteristic has allowed us to create a strong clear signal dominated by passage formation in a surfactant sponge of cetylpyridinium chloride/hexanol membranes in a solution of brine with an inert dextrose thickener. This viscous solvent slows the dynamic response of the sponge phases, allowing experimental access to the interplay between structure and dynamics over a wide scale range. Under applied Couette shear sponges in this system can be easily be transformed to lamellar phase stacks of membrane. When flow stops all the passages in this such a shear-induced lamellar phase must reform to re-establish the sponge equilibrium topology.

We can measure this overall structural relaxation using time-resolved small angle neutron scattering (t-SANS). Comparing this time to the interval between diffusive membrane contacts - which may be determined from dynamic light scattering (DLS) measurements or more simply estimated from the shear rates required for shear-induced lamellar saturation - allows us to determine the activation energy barrier to membrane fusion at each contact.

Some aspects of the intermediate structure which gives rise to this energy barrier may be deduced from its variation in samples with a range of membrane volume fractions or intrinsic membrane curvatures, with implications for theoretical models of membrane passage formation.

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STRUCTURE OF FUNCTIONAL TOXIN PORES IN TETHERED BILAYERS: MEMBRANE ASSOCIATION OF HEMOLYSIN

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The toxin α -hemolysin (α HL) from *Staphylococcus aureus* is a paradigm of a pore-former in biomembranes. The protein has been extensively investigated in single-molecule electrophysiologic studies of free-standing membranes, its atomic-scale structure has been solved by X-ray crystallography, and the suggestion to use the molecular pores in DNA-sequencing devices has received considerable attention. Aiming at both structural studies of its membrane incorporation, and the development of the protein into a sensor format with long-term stability, we demonstrate the reconstitution of these toxin pores in a biomimetic tethered bilayer membrane (tBLM) on a solid substrate which we have developed and optimised.

The electrical characteristics of the pore, determined from electrical impedance spectroscopy, are consistent with measurements of functional proteins in free-standing lipid membranes while being stable over long periods of time (days). Neutron reflectometry shows the protein's cap domain at high density outside the bilayer membrane, and significant impact of the protein on the head group region of the outer membrane leaflet. A more sophisticated analysis of the neutron data using the known X-ray crystal structure of the protein gives detailed structural information about the interaction of the protein with the membrane. This work has established the practicality of obtaining specific structural information from functioning membrane-incorporated proteins, leading to further studies including work on diphtheria, anthrax and tetanus-derived proteins.

MOLECULAR STRUCTURES OF POLYMERS AND BIOLOGICAL MOLECULES AT INTERFACES

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Molecular structures of polymers and biological molecules such as proteins and peptides play important roles in biocompatibility, anti-biofouling control, adhesion, membrane protein function, biosensing, and anti-microbial peptide behavior. Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular structures of polymers, proteins, and peptides at the solid/liquid interface in situ in real time. SFG studies on polymer materials reveal molecular level details regarding polymer surface restructuring in water and polymer adhesion. SFG results of biological molecules demonstrate that C-H stretching and amide signals can elucidate structures of hydrophobic side chains and secondary structures of interfacial peptides and proteins. Time-dependent structural changes of adsorbed proteins at the solid/liquid interface have been monitored. Adsorbed protein structures have been correlated to blood coagulation behavior on the surface. Lipid bilayers have been used as models for cell membranes to elucidate molecular interactions between cell membranes and antimicrobial peptides as well as some simple antibiotic compounds. Membrane protein orientation has been elucidated using SFG. This research demonstrates that SFG is a powerful technique which can elucidate molecular structures of polymers, proteins, and peptides at interfaces in situ. Several supplemental techniques including ATR-FTIR, QCM, four-wave mixing vibrational spectroscopy, and contact angle goniometry have been used in the research to substantiate the SFG results.

A NANOSCALE GAS STATE

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We show that a very thin (5~80 nm) gas phase can exist for hours at the interface between a hydrophobic solid and water at ambient pressure and temperature. We create the gas phase from CO₂, which allows us to determine the chemical identity and phase state via infrared spectroscopy. The nanoscale dimensions were determined by atomic force microscopy (AFM), and the low refractive index of the layer was confirmed by surface plasmon resonance (SPR). Spectroscopic measurement of the average density reveals that the gas is at approximately atmospheric pressure, which explains the unexpectedly long lifetime of the phase under ambient conditions. The nanoscale gas phase is easily and reproducibly created under conditions where gas solubility is varied.

IN SITU IR STUDIES OF THIOL LIGAND ADSORPTION ON CdS FILMS

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Quantum dots (QDs) are sufficiently small crystals of a semiconductor material such that their emission properties (eg. wavelength) become size dependent. Typical QD materials readily oxidise in ambient environments and are often capped with a higher band-gap material to prevent such degradation. Further capping with bi-functional ligands can solubilise the nanocrystal in different environments and/or expose functional groups for further chemical reaction. Probing the surface chemistry of thiol ligand binding to cadmium chalcogenide nanocrystals is important to clarify factors involved in QD stability and surface functionalisation.

Deposited CdS nanocrystal films have been used in this work as model QD surfaces for ligand adsorption studies. The adsorption of mercaptoacetic acid, mercaptopropionic acid, and mercaptoethanol, from aqueous solution to CdS thin films has been studied by *in situ* infrared spectroscopy.

The kinetics of adsorption of these three ligands under various conditions has been studied. The adsorption of a ligand from solution increases with time until a point where surface saturation is obtained. The rate constant for adsorption (k_a') has been found to depend on pH and to a lesser degree ionic strength. The trends observed are rationalised in terms of CdS surface charge and the ionic kinetic salt effect. Introducing a new solution in the absence of any ligand allows the desorption process to be monitored. The rate constant for desorption (k_d') shows less variation with experimental conditions. This adsorption/desorption process is shown in Figure 1.

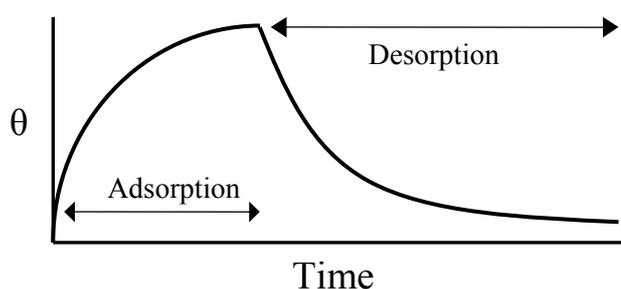


Figure 1. A plot showing a ligand adsorption/desorption process to a surface.

An expression relating the constants k_a' and k_d' to the Langmuir affinity constant (K_L) can be obtained. K_L values can therefore be obtained without the time consuming equilibration of various concentration solutions as is required when employing the conventional adsorption isotherm approach. The relative merits or otherwise of employing this method of obtaining K_L values will be discussed. The K_L values obtained for these ligands on CdS films compare favourably to those obtained by the traditional approach.

PROBING THE CATION EXCHANGE CAPACITY AND BIOMINERALISATION PROPENSITY OF BACTERIAL SURFACES WITH *IN SITU* IR SPECTROSCOPY

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Bacterial surfaces in neutral solution carry considerable cation concentrations due to the existence of anionic functional groups such as phosphomonoesters, phosphodiester and carboxylates. The capacity of bacterial surfaces to sequester cations has led to explanations of the existence of fossil records for ancient bacteria and have provided hopes for the use of bacteria as bioreactors for remediation of heavy metal contaminated urban waste. Better knowledge of the cation exchangeable sites and of the cation exchange processes in live bacteria are needed to translate bacterial bioreactor hopes into practicable applications.

Most of what we know about the chemical composition of bacterial polymeric appendages comes from *ex situ* analysis of hydrolysis products but extrapolation of this information to infer the surface chemical behaviour of live bacteria has limitations. The existence of the proton motive force in live cells maintains local proton concentrations at cell membrane surfaces which are different from those in the bulk solution. This is reflected in zeta potential measurements which differ for live and dead cells and bring into question inferences from such data about surface charge and surface functional groups. Such differences also exist between the cation exchange properties of live and dead cells. These differences reflect the spatial distribution of the bacterial surface anionic charges which is mostly poorly defined. However, for the Gram negative bacterium *Pseudomonas aeruginosa* the lipopolysaccharide structure of the bacterial surface envelope is well established.

We have worked with *Pseudomonas aeruginosa* and with two of its mutants having different extents of truncation of the lipopolysaccharide extensions to the cell wall. In particular, we have used *in situ* internal reflection IR spectroscopy to examine “monolayers” of live bacteria and, by changing pH, to reveal the functional groups influencing bacterial surface charge. We have also carried out cation exchange experiments with live and dead cells to evaluate the influence of the proton motive force on the spatial distribution of cation exchange within the cell wall structure. The relevance of our findings to cation exchange capacity and biomineralisation propensity will be discussed.

THE SURFACE CHEMISTRY OF SINGLE NANOCRYSTALS

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This talk will provide an overview of our recent research into the spectroscopy and surface chemistry of single semiconductor and metal nanocrystals.

In the first part of the talk, we focus on the possibility to study the optical properties of single metal particles using dark-field microscopy. It is now possible to routinely collect the scattered light from single metal nanocrystals and use this to study the effects of particle size and shape on the surface plasmon (SP) resonances. We show that the linewidth and energy of the SP resonance is acutely sensitive to the particle end cap geometry, to the aspect ratio and to atomic roughness on the particle surface. We demonstrate that electron injection causes colour changes in single particles.

In the second part of the talk we discuss the phenomena of blinking and spectral diffusion in the luminescence collected from single semiconductor nanocrystals and its origins. We demonstrate that the Auger mechanism often postulated to account for blinking and spectral diffusion is inconsistent with observations. Instead we propose that surface recombination can account for many of the unusual effects observed. By passivating the crystals with thin shells of a second semiconductor, we find that we can completely passivate the crystal and produce an ideal two level system.

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ORGANIC SYNTHESIS OF FLUORINATED MOLECULES ON GaAs(100) AND Cu(100)

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The adsorption of trifluoroethane thiol (TFET) on GaAs(100)-(4x1) and Cu(100) surface has been studied using temperature-programmed desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS).

Surface studies of TFET show that it adsorbs on GaAs(100) at 111 K with complete dissociation of the S-H bond to form thiolate species ($\text{CF}_3\text{CH}_2\text{S}^-$). Partial C-S bond scission is also observed to produce CF_3CH_2^- species. These surface species undergo several competing reaction pathways leading to the formation of $\text{CF}_3\text{CH}_2\text{SH}$ (recombination), $\text{CF}_2=\text{CH}_2$ (β -fluoride elimination), CF_3CH_3 , and H_2 (hydrogen reduction) and $\text{CF}_3\text{CH}_2\text{CH}=\text{CF}_2$ (coupling product). Furthermore, fluorine (from β -fluorine elimination) migrates into the sub-surface producing GaF_x species. These GaF_x species etch spontaneously from the surface and displace arsenic to the surface which desorbs as As_2 .

Similarly, TFET adsorbs on Cu(100) at 101 K to dissociate and form thiolate and alkyl species. These species undergo additional reactions including the coupling product, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$. Further work has investigated co-adsorption of two alkyl species on Cu(100) to produce new coupling product. The reactions of propyl groups with CF_3CH_2^- species produced the coupling product, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. These results indicate that selective growth of long chained is possible through the choice of precursor molecules.

THE COMPETITIVE SWELLING KINETICS OF THIN POLYSTYRENE FILMS BY TOLUENE.

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Thin polymer films on solid supports are used in many important technical applications, such as those involved in lithographic processes in the microelectronics industry. Typically, these films are exposed to a gas atmosphere and molecules from this atmosphere are incorporated inside the thin polymer film. The absorption of gasses from our atmosphere such as carbon dioxide and exhaust fumes into polymers has non negligible implications for the material properties of polymers materials.

Here we discuss the competitive penetration of toluene with respect to normal atmospheric gases (O₂, N₂, CO₂) into a thin film of polystyrene. In-situ neutron reflectometry is an ideal technique for studying the swelling of such films, gaining important information on possible diffusion models from the swelling and de-swelling kinetics.

DETERMINATION OF THE PHYSICO-CHEMICAL PARAMETERS AND AGGREGATION NUMBER OF SURFACTANT IN MICELLES IN BINARY ALCOHOL-WATER MIXTURES

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One method of investigating the hydrophobic interaction between the hydrocarbon chains of a surfactant and solvent water molecules is to alter the structure of the water by modifying the solvent composition, and then observe the effect of this modification on micellar aggregation. The simplest way to alter the water structure is to add a co-solvent such as an alcohol, dioxane, or glycerol.

In the present work, the effect of ethanol on the micellization of the anionic surfactant, sodium dodecyl sulfate (SDS), was investigated using potentiometric and Pulsed field gradient-NMR spectroscopic techniques. Potentiometry studies showed that the critical micelle concentration (CMC) of surfactant decreases to a minimum value at around 10% ethanol (v/v) because of the co-surfactant effect. The mean values of the hydrodynamic radius, R_h , and aggregation number, N_A , of micelles were determined by a combination of viscosity and self-diffusion coefficient measurements. The viscosity of the micellar solutions was approximately independent of ethanol concentration, indicating that the presence of the alcohol does not induce substantial changes in the micellar structure. The number of attachment of ethanol in the micellar core and the degree of dissociation of the counter ion were evaluated using a potentiometric technique for alcohol concentrations between 5% to 40% v/v. In addition, an explicit expression is developed for the average size of micelles formed in aqueous solvents containing alcohol.

MIXED MONOLAYER AND MICELLE FORMATION OF CATIONIC AND ZWITTERIONIC SURFACTANT OF IDENTICAL HYDROCARBON TAIL IN AN AQUEOUS MEDIUM: INTERFACIAL TENSION, FLUORESCENCE PROBE, DYNAMIC LIGHT SCATTERING AND VISCOSITY STUDY

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Mixed monolayer and the micelle formation of cationic and zwitterionic surfactants, dodecyltrimethylammonium bromide (DTAB) + dimethyldodecylammoniopropanesulfonate (DPS), have been studied by interfacial tension, fluorescence, dynamic light scattering (DLS), and viscosity (η) measurements. According to the Clint and regular solution approximation theories, the interaction parameters in the mixed micelle (β_{12}^{mic}) and in the mixed monolayer (β_{12}^{σ}) have been evaluated at the different mole fraction of DTAB (α_{DTAB}). The value of micelle composition (X_1) and monolayer composition (X_1^{σ}) at different α_{DTAB} indicates that the mixed micelles and the mixed monolayer are lower in DTAB content as comparison to DPS.

By using static fluorescence quenching method, the mean micellar aggregation number of pure and mixed micelles was obtained. Rigidity of pure and mixed micelles was observed from the fluorescence anisotropy (r) measurements by using a probe Rhodamine B. It has been observed that the value of r for DPS is higher than those of DTAB indicating the presence of compact and rigid micelle of DPS and r value decreases with the increase of α_{DTAB} indicating that the induction of DTAB into the DPS micelle creates electrostatic repulsion to produce loose mixed micelle. The diffusion coefficient of micelle was obtained from DLS measurements. These results directly correlate with the fluorescence anisotropy. Viscosity measurement shows the minimum at a different α_{DTAB} and this minimum is shifted to a high α_{DTAB} depending upon the total concentration of surfactant mixture. This minima maybe shows the some kind of structure transition of the micellar structure as shown in Fig.1.

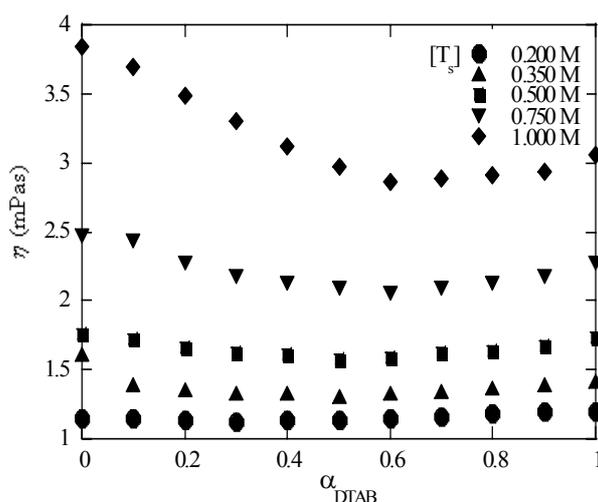


Fig. 1. Plots of viscosity vs. α_{DTAB}

FRICIONAL PROPERTIES OF CONFINED NANOPARTICLES: EFFECTS OF PARTICLE SIZE AND SHAPE

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Nanoparticles have long been considered as suitable candidates for lubricants due to their presumed ability to roll like ball bearings between two shearing surfaces. Some nanoparticles have provided significant improvement as dry lubricants. We report the results of a series of experiments on various nanoparticles suspensions. We find that surfactant-coated nanorods, rather than bare spheres, provide both low friction and good surface wear protection when used as additives in fluids that are not good lubricants on their own. We have investigated some of the conditions that optimize tribological performance over a large range of loads and sliding speeds—obtaining friction coefficients of ~ 0.04 over a large range of sliding speeds up to pressures in excess of 200 MPa. We propose that the superior properties of nanorods are due to a combination of the nanoparticle geometry (short rods rather than spheres or wires), nanoparticle stiffness (hard, robust cores with soft outer layers), and soft nanoparticle interactions (weakly adhesive inter-nanoparticle and nanoparticle-surface forces due to a synergy between the nanoparticle cores, the surfactant layers, the solvent, and the moving surfaces). Such judicious manipulations of the structure and colloidal forces of non-spherical nanoparticles should allow for the rational design of low friction, surface-protecting additives in both oil- and water-based systems.

THE INFLUENCE OF CYCLOHEXANE VAPOR ON STICK-SLIP FRICTION BETWEEN MICA SURFACES

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The stick-slip friction between mica surfaces under cyclohexane vapor was investigated with the Surface Force Apparatus (SFA). The dynamic shear stress decreased from 60MPa to 10MPa with increasing the relative vapor pressure (r.v.p.) from 5 to 50%. Between the r.v.p. of 50 and 80%, the shear stress remained around 10MPa, with a slight decrease on increasing the r.v.p. At r.v.p. greater than 80%, the values of shear stress were below 5MPa.

The stick-slip behavior was observed in the range of r.v.p. from 20% to the saturation. When the r.v.p. reached 20%, the stick-slip appeared but faded out with sliding time. At the r.v.p. greater than 50%, the stick-slip pattern was stable without fading.

With taking into account the size of the meniscus formed by capillary condensation of the liquid around the contact area and the Laplace pressure, the dependence of shear stress and the stick-slip modulation on r.v.p. suggests that the origin of the stick-slip observed in cyclohexane vapor is as follows:

At the r.v.p. greater than 50%, where stable sick-slip is observed, the stick-slip caused by the cyclohexane layering in the contact area is of essentially the same origin as observed with mica surfaces sliding in bulk cyclohexane liquid. Like for the bulk liquid experiment, decreasing the layer thickness (or the number of the layers) between the surfaces increases the shear stress at the slip onset. In the vapor phase experiments, the stick-slip is enhanced by the increase of the negative Laplace pressure in the capillary condensed liquid with decreasing the r.v.p., forcing the surfaces stronger toward each other.

In the range of r.v.p. between 20-50%, where the fading stick-slip is observed, the liquid condensed seeps into the contact area by the applied tangential force, and thus triggers the slip motion. Due to the small condensation volume, the liquid condensed around the contact area is exhausted in the process of repeating stick-slip. As the slip length is limited to the meniscus size, stick-slip amplitude gets smaller, and eventually the surfaces start sliding without stick-slip.

INTERACTIONS BETWEEN SUPPORTED PHOSPHOLIPID BILAYERS AND SILICA SURFACES

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Supported phospholipid bilayers (SPBs) have received considerable attention as models of cell membranes, for their ability to biofunctionalize inorganic surfaces, immobilize proteins on surfaces and for their promise as a platform for biosensors and other diagnostic devices. A common method of making SPBs is through the spontaneous adsorption, rupture and spreading of vesicles from solution onto a solid substrate. The process, commonly called vesicle fusion, is highly dependent on the vesicle-substrate, and vesicle-vesicle interactions. Recent work has begun to shed light on the nature of the vesicle fusion process; however a clear understanding of the fundamental vesicle-substrate interactions is still needed.

We have used a variety of techniques to study the vesicle fusion process and elucidate the nature of the vesicle-substrate interaction. A Surface Forces Apparatus (SFA) has been used to probe the force-distance profile of a phospholipid bilayer supported on mica with an amorphous silica surface in aqueous solutions. We have found in addition to the van der Waals attraction, an electrostatic attraction between the two dissimilar surfaces as well as the stabilizing repulsive forces are important in determining the overall bilayer-silica interaction and adhesion energy. Quartz crystal microbalance and ellipsometry techniques have been employed in conjunction with the SFA results to study the bulk vesicle fusion process. The results have contributed to a better understanding of the vesicle fusion mechanism and will be important in any application of SPBs.

NANO-TRIBOLOGY OF CLEAN HYDROPHILIC SILICA SURFACES IN ELECTROLYTE SOLUTIONS OF NORMAL AND HIGH pH'S

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We conducted very carefully a series of AFM measurements of normal and lateral forces between completely-hydrophilic silica surfaces in various electrolyte solutions of normal and high pH's, and found that the friction behaviours are classified into 4 Cases illustrated below.

In the case of normal pH, the lubrication was observed for solutions of mono-valent cations as shown in Case A, although the degree of lubrication depends on the kind and concentration of cations. As for the divalent cations, the transition from Case A to Case B was found with increasing hydration enthalpy of cations. In the case of trivalent cations, the behaviour was classified as Case B. It was also found that the anions play an important role in this case.

In the case of high pH, the surfaces were hairy-like and elastic. It was found that (1) the relation of the friction F_L vs. the loading force L is non-linear, (2) whether the friction behaviour is classified as Case C or D depends on the adhesive property of adsorbed layers of cations on the hairy-like surfaces. The interesting relation of F_L vs. v shown in Case B and D was explained theoretically. The details will be given in the talk.

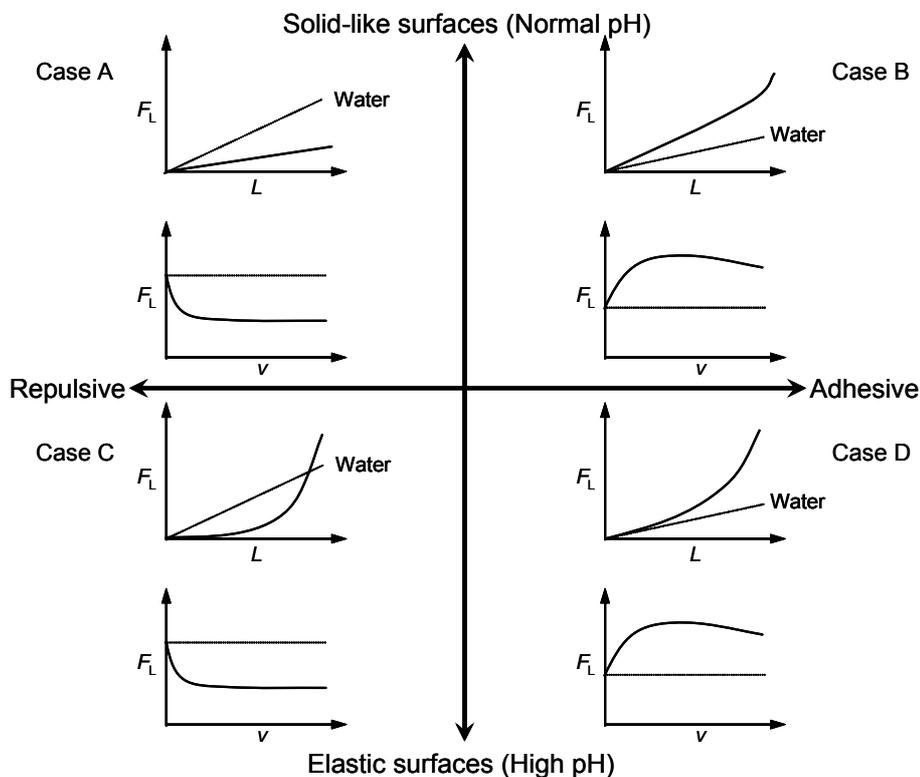


Figure Classification of the dependence of the friction force F_L on the loading force L and the scan rate v . ("Water" indicates the reference friction for water.)

EVAPORATION-STABILIZED FOAM FILMS OF PURE LIQUIDS

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It is commonly recognised that pure liquids do not form stable films. For a range of ordinary organic solvents we did indeed observe instant coalescence of bubbles when the air is vapour-saturated. However, at surfaces of evaporating ethanol and other volatile liquids bubbles stay for an extended period of time.

We have studied the evaporation inhibition of bubble coalescence using a film balance featuring, in provision for dynamic studies, low flow resistance along with hydrostatic pressure, gas flow and vapour saturation controls. The film was monitored in monochromatic light with a videomicroscope. As an example, the Figure below shows an interference pattern observed with an ethanol film in free evaporation.

Because of the quasi-adiabatic conditions following from the thermal insulating properties of air adjoining the two surfaces and the small mass of its body, the liquid film cools faster through the evaporation than the surface of the surrounding bulk liquid. The emerging surface tension gradients drive the liquid circulation inwards, towards the middle of the film, counteracting the drainage out.

We consider the dynamic patterns of laminar and turbulent circulation with varying molecular nature of the liquid, vapor saturation and gas convection conditions. The physical mechanism of the evaporation inhibition of bubble coalescence is verified through a dimensional parametric analysis incorporating the latent evaporation heat, heat capacity and conductivity, viscosity and surface entropy. A comparison is made with the static stability of symmetric liquid films due to surface charge and surface freezing, solute and phase inversion Marangoni effects.

Figure: A snapshot of an evaporating film of ethanol
The dynamic relief shows a circulation summit,
closer to one side of the ~1 mm diameter film,
and three flow inlets at the opposite side.
Between each two adjacent constant intensity lines
the thickness of the film changes in 295 nm increments,
half the wavelength of the illuminating light (sodium lamp)



ELECTROWETTING IN A NANOPORE

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We carried out the first and thorough molecular modelling study of electro-wetting in a nanoscale regime. Traditionally, electro-wetting has been considered a relatively non-specific phenomenon defined in terms of a material's macroscopic properties. In the nanoscale regime, where surface molecules represent a significant constituency, however, the competition between spontaneous water molecule-surface orientations, and molecular dipole alignment in the field can play a major role. Our simulations of wetting/dewetting equilibrium, along with the ensuing analysis of hydrogen bond populations, demonstrate a surprisingly strong effect of field direction and polarity on nanopore-surface affinity for water. This new phenomenon is potentially relevant to surface manipulation in microfluidics, as well as for basic understanding of field charge effects that modulate local hydrophilicity of engineered and biophysical surfaces (supported by US National Science Foundation).

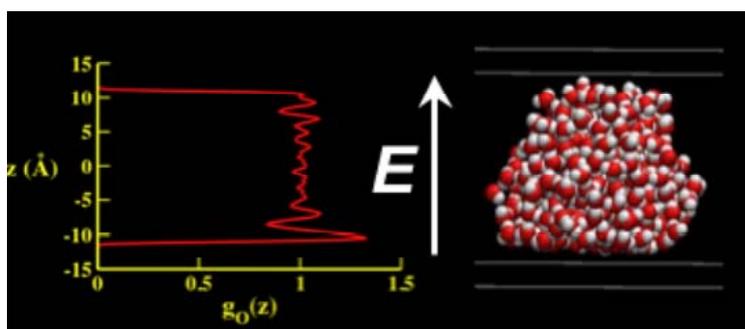


Figure: When electric field is applied in the direction perpendicular to the confining hydrophobic surfaces, the competition between field-induced alignment and orientational preference of interfacial water molecules relative to the surfaces results in *asymmetric* wettability of opposing surfaces.

DYNAMICS OF CAPILLARY-HELD LIQUIDS

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Capillary condensation of a wetting liquid from undersaturated vapor is perhaps the best known example of a surface-induced phase transition, and plays an important role in determining the behavior of systems ranging from hard disk drives to sand castles. Here we present the results of Surface Forces Apparatus experiments on the formation and disappearance of capillary-held liquids, with an emphasis on dynamics. The observed condensation rates are consistent with a model which takes into account both vapor diffusion and flow in thin liquid films adsorbed on the pore surfaces. Furthermore, our measurements reveal the presence of two distinct modes for the disappearance of liquids held in a slit-like pore of adjustable slit-width, dependent on the slit-opening rate. In contrast to the first mode ('bridge rupture'), which is well-documented in terms of the Young-Laplace equation, unexpected behavior was observed in the second mode ('evaporation'), where the liquid bridge was held in the vicinity of the thermodynamic phase boundary (equilibrium Kelvin length). We will discuss potential implications of these results in the behavior of a wide range of systems.

FORCE SPECTROSCOPY WITH AFM: SURFACE CHARGE OF SPECIFIC BARITE CRYSTAL FACES

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It has long been recognised that surface charge is an important physical property of colloidal particles. However, the measurement of this property is not always straightforward. The standard method of measuring zeta potential gives only an average value for the entire surface of the particle and it is well understood that different crystal faces should have different surface charges due to the different ions that are exposed to the solution. In this work we show how the AFM and its force spectroscopy capability can be used to gauge surface charge for a single and particular face of barite in solution.

Barium sulphate was chosen as the substrate of interest as it is useful as a model precipitating system due to its low solubility, simple chemistry and lack of polymorph formation over a wide range of conditions [1]. It is also a common scale compound and as such has been the focus of many investigations into scale forming materials [2-4].

In the present study barite particles of known morphology were glued to AFM cantilevers using the AFM system as a nano-manipulator (see Fig. 1). These modified cantilevers were then used for force measurements in solution between various crystal faces. The measured force is non-trivial, incorporating both attractive and repulsive contributions. We present here a first attempt at extracting this important information in colloidal and nano-chemistry. In addition, an overview of the facilities available at Curtin University of Technology will be given with some examples of the work currently being conducted.

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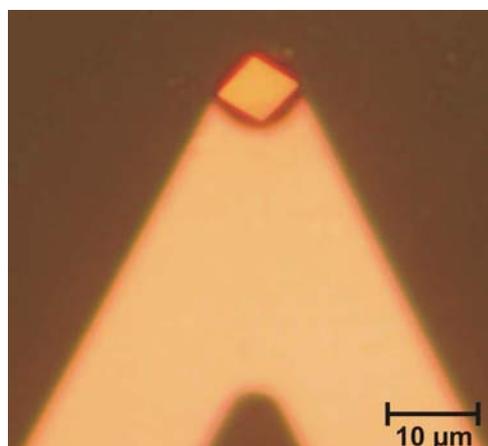


Figure 1: Barium sulphate particle ((001) face) fixed to an AFM cantilever.

EFFECTS OF SURFACE FORCES ON A TORSIONAL ULTRASONIC OSCILLATOR

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There has been much recent interest in cohesive microfluidic surface forces under variable conditions of wettability, surface chemistry or roughness. In particular, little is known about the influence of these factors on finite slip at the fluid-surface boundary. Some of the most successful experimental investigations of slip have been carried out using force measurement devices such as atomic force microscopes, surface force apparatus and MHz quartz crystal resonators. A novel experimental technique has been developed for investigating surface forces between a fluid and the surface of an ultrasonic oscillator. The technique has advantages over other methods because two independent values of the oscillation Q-factor are measured. Using these two measurements, calibration of the system is verified and the phase-dependent origin of any forces can be inferred.

The system consists of a composite torsional ultrasonic oscillator constructed using piezoelectric quartz rods (see figure). A specimen rod is set oscillating at 40 kHz with controllable strain rate ranging from 50 s^{-1} to $\sim 10^4 \text{ s}^{-1}$ and linear displacement amplitude from less than 1 nm to $\sim 150 \text{ nm}$. The system is configured for independent measurement of the oscillation frequency and the ratio of the piezoelectric voltages across the drive and gauge crystals. When an oscillating specimen is immersed in a fluid of interest, microfluidic cohesive forces control the damping that occurs. Damping of the oscillator can be precisely characterized by considering an 'equivalent circuit' that describes the combined mechanical and electronic parts of the system. Analysis of the cohesive forces yields a quantitative value for slip length. The apparatus will initially be used to investigate the effect of changing wettability and surface roughness on coated, polished quartz specimen rods.

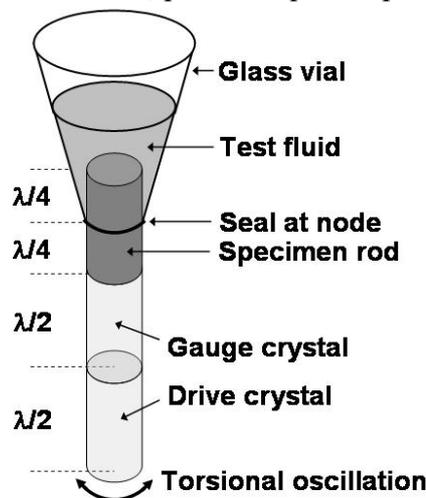


Figure: Diagram of the composite torsional oscillator, consisting of two identical cylindrical piezoelectric quartz rods and a specimen rod of the same resonant frequency. A standing torsional oscillation (wavelength λ) can be induced in all three rods by applying a voltage to the drive crystal. Displacement antinodes are located at free ends and joints.

MODELING ION-SPECIFIC COLLOIDAL AND PROTEIN INTERACTIONS

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Addition of salts is commonly used to manipulate interparticle forces and phase equilibria in solutions of proteins, colloids, and nanoparticles. In addition to nonspecific screening effects, salt ions interact with colloidal solutes through strongly specific dispersion forces. Using an integral-equation approach, we estimate the role of these forces on inter-colloidal correlations and phase behavior of solutions of ionized nano-sized solutes. Dispersion potentials between ionic species in saline colloidal solutions are calculated from the Lifshitz theory and measured ion polarizabilities along with estimated ionization energies in aqueous medium. These potentials are employed in an approximate integral equation theory to study ion-sensitive macroion pair potentials of mean force and spatial correlations among colloids and salt ions. Effective intercolloidal potentials are exploited in MacMillan-Mayer level calculations of phase diagrams of the dispersion using the 2nd order perturbation approximation. Theoretical predictions are validated by comparisons with parallel computer simulations of salt-dependent interprotein forces and measured thermodynamic data for aqueous lysozyme solutions.

For realistic solution conditions, ionic polarizabilities are demonstrated to represent significant and predictable determinants of the solution phase behavior with overall influence often comparable to that of Coulombic interactions. Our calculations show that van der Waals ion-macroion forces represent a major and likely the dominant contribution to the observed salt dependence exemplified by the celebrated Hofmeister scale. While a complete account of ion-specific effects on colloid phase diagrams clearly requires the inclusion of molecular solvent interactions, our theoretical framework provides a useful guidance in designing separation processes where a salt is used to induce colloid or protein precipitation.

PARTICLE-PARTICLE AND PARTICLE-SUBSTRATE INTERACTIONS IN COLLOIDAL SELF-ASSEMBLY

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Colloidal self-assembly has gained significant research interest due to its application potential in photonic/phononic crystals, bio-/chemo-sensors, tissue engineering, as well as in fundamental studies of crystal formation and melting. Among many methods developed for the preparation of colloidal crystals, vertical lifting deposition is widely used owing to its simplicity and ability to produce crystals of high order and quality. Studies have been carried out to search for a set of optimal operational parameters for creating large crystal areas with minimum defect densities and controllable thickness by tuning suspension concentration, lifting velocity, humidity, drying speed, and surface patterning. Although it is well recognized that liquid-mediated forces, such as the capillary force, are key driving forces in colloidal self-assembly and affect the final crystal quality, other factors such as van der Waals and electrostatic forces based particle-particle, particle-substrate interactions that also play a role in the process, are much less understood.

This study presents a systematic investigation to address this less active area. Colloidal crystals have been fabricated through vertical lifting depositions with varied surface electric potential and functional groups of both the particles (polystyrene and silica core-shell particles via synthesis route), and substrates (by coating aminopropyltriethoxysilane (APTE) and N-trimethoxysilylpropyl-N, N, N-trimethyl-ammonium chloride (NR_4^+) on glass slides). The resulting colloidal crystals are characterized by their morphology such as thickness, defect density, as well as by their light diffraction property through UV-vis absorbance spectra. Atomic force microscopy (AFM) was employed to characterize the interactions between such particles and substrates. A link connecting the colloidal crystal quality and particle-particle, particle-substrate interactions are extracted from this study.

FORCED DESORPTION OF SURFACTANT AT POLYMER – WATER INTERFACE

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Polymer film formation from an aqueous colloidal latex modifies the surfactant distribution at the polymer – water interfaces and in their vicinity, particularly in the latest steps of the drying process. The Surface Force Apparatus (SFA) technique provides an avenue to investigate the drying process of lattices, as the aqueous gap can be decreased in a controlled approach of two opposite curved polymer surfaces immersed in aqueous surfactant solutions.

Stable polymer surfaces are deposited by spin coating on mica with a surface roughness less than one nanometer. Equilibrium adsorbed surfactant structures made of sodium dodecylsulfate (SDS), on the poly (ethyl methacrylate) (PEMA) coated mica surface are determined by AFM imaging in aqueous solutions. Surfactant molecules adsorb as flat pancakes no higher than a hemi-micelle but with lateral extension about an order of magnitude larger than the bulk micellar diameter. Over the bulk surfactant concentration range $1/10^{\text{th}}$ to 10 c.m.c., the adsorbed aggregates keep their size almost constant while their surface density increases with concentration above the c.m.c. These two surface coverage regimes are coherent with the SFA studies where a direct forced desorption of surfactant aggregates is observed only over the low bulk concentration range (below the c.m.c.). The adhesion between the surfaces is indeed facilitated by the hydrophobicity of the polymer – water interface (cavitation).

The measurements on this model system are compared with fluorescence depolarization experiments coupled with torsion resonator measurements performed on a butyl acrylate/ methyl methacrylate latex containing 4% of acrylic acid (soft particles as $T > T_g = 15^\circ\text{C}$). Independent of the SDS surfactant concentration, the film drying kinetics is composed of two regimes: a slow drying followed by an acceleration. This dynamics correlates well with the SFA results where it is suggested that the cavitation formation between latex particles allows their interfaces for approaching upon the drying film process. Thus the water evaporation during the drying of a latex film causes total or partial desorption of surfactant by confinement, this being due to the surfactant adsorption distribution on the local chemical or structural heterogeneities existing at the polymer-water interfaces.

DIRECT MEASUREMENT OF INTERACTIONS BETWEEN SURFACE-GROWN POLYMER BRUSHES IN AQUEOUS MEDIA

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If polymers are end anchored on the solid surface at a sufficiently high density, with their chains stretching into the surrounding medium, they form a brush-like structure. The understanding of such polymer brushes has important implications to colloidal stability and various biological processes. In the conventional “grafting to” strategy to form polymer brushes, end-functionalised polymers are adsorbed on the surface from a solution. However, this strategy has several limitations: for example, the relatively weak anchorage (typically a few $k_B T$) thermodynamically limits the brush grafting density, and the brush formation may also be kinetically hindered.

A more recent alternative “grafting from” strategy is to grow polymer brushes directly from the solid surface. In this study, we have adapted this synthesis strategy to the mica surface, and report the growth of a water soluble pMPC (poly(2-methacryloyloxyethyl phosphorylcholine)) brush on mica. This enables the direct measurement of surface forces and friction between the obtained brushes in aqueous media, using a version of the interferometric surface force apparatus with mica as substrates. Our results reveal a deviation from the Alexander-de Gennes description of the brush interaction at high compressions, and very low frictional forces between the brushes. We will relate briefly to the possible implications of our results in a biolubrication model, in which various biomacromolecules on tissue surfaces are thought to mediate “frictionless” sliding between them.

Acknowledgement: S.P. Armes, A. Lewis & H. Cohen

BRIDGING OR DEPLETION – IS THAT ALL THERE IS? “NEW” MECHANISMS OF DESTABILISATION OF AQUEOUS POLYMER-PARTICLE MIXTURES

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Aqueous mixtures of flexible polymers and colloidal particles are ubiquitous in applications such as foods, paints, pharmaceutical products, and papermaking. Two mechanisms of destabilisation of mixed polymer-particle solutions are commonly recognized: Depletion (for repulsive polymer-particle interactions) and bridging (for attractive polymer-particle interactions). However, a third type of mechanism may operate in cases where the particle-free polymer solution by itself is close to phase separation. In such cases, a capillary-induced phase separation may occur in the gap between neighbouring particles, giving rise to an attractive force between the particles. Recently, this type of force was discovered between surfaces immersed in two types of phase-separating polymer solutions: A “clouding” solution of ethyl hydroxyethylcellulose (EHEC) [1], and a classical segregating mixture of poly(ethylene oxide) (PEO) and dextran [2].

Inspired by the above force studies, we have continued to study how added particles influence the clouding of EHEC solutions [3] and the phase separation in mixtures of dextran and PEO in water [4]. Small additions of particles can hugely increase the tendency for phase separation, and the magnitude of the effect depends on the nature of the particle (silica or polystyrene latex), and on the concentration of added salt. Two mechanisms, outlined below, seem to operate.

- In the EHEC solutions [3], and close to the binodal of the PEO-dextran-water mixtures [4], the phase separation mechanism is closely related to a capillary-induced phase separation.
- At low concentrations of PEO, adsorption of PEO strongly changes the surface characteristics of the particles. This results in a repulsion between dextran and the PEO-dressed particles [4].

The experimental findings are qualitatively predicted by mean-field lattice calculations [5-7].

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LIQUID STRUCTURING INDUCED BY SOLID SURFACE: HYDROGEN-BONDED SURFACE MOLECULAR MACROCLUSTER

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Adsorption at the solid-liquid interfaces from binary liquid mixtures is one of the important adsorption system because the elucidation of properties and structures of the liquid adsorption layers on solid surfaces is becoming increasingly important in advanced materials science and technology in nanometer scale. However, the understanding of such phenomenon was remained at the macroscopic level. Recently we investigated liquid adsorption onto silica surface from binary liquid mixtures of polar and non-polar liquids such as alcohols (carboxylic acids, amides)–cyclohexane using colloidal probe AFM, ATR–FTIR spectroscopy and adsorption excess isotherm measurement. We found that alcohols, carboxylic acids and amides adsorbed on the silica surface form ordered structures extending to several tens of nanometer through hydrogen bonding (Fig. 1, surface molecular macrocluster).^{1–7} Surface forces measurement revealed that the long range attraction appears from distances about twice of the macrocluster layer thickness, indicating that contact of the adsorption layers brings about the long range attraction.

In this study, the interfacial energy (γ) was estimated by analysing the attraction based on the model shown in Fig.1.⁷ The surface forces between glass surfaces in methanol–cyclohexane binary liquids are shown in Fig.2 together with the estimated γ . The γ values for 0.03 and 0.16 mol% methanol were 10 times larger than the γ value for methanol/cyclohexane in phase separation (0.6 mN/m). This large γ should be arisen from the rather fixed terminal free OH group of linear methanol macrocluster chain. As a comparison, the surface forces between glass surfaces were measured

at methanol concentration of 9.1 mol% (above phase separation ca.8 mol%). The attraction suddenly appeared from a distance of ca. 800 nm and almost constant until contact. The γ value estimated from the adhesion force was 0.6 mN/m, which agreed well with literature value. This completely different interaction force and weak γ obtained above phase separation indicates that the molecular macrocluster formation is not related to the phase separation, and a surface induced phenomenon.

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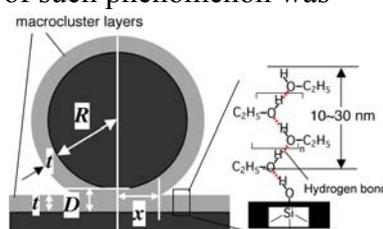


Fig. 1. Schematic illustration of bridging of macrocluster layers (alcohol macrocluster).

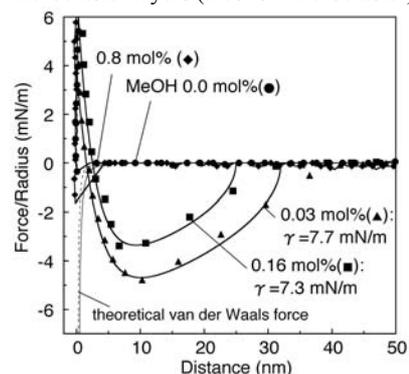


Fig. 2. Surface forces between glass surfaces in methanol–cyclohexane binary liquids and the fitting curves.

INSTABILITIES IN THE INTERACTION OF SURFACES COATED WITH THIN LIQUID FILMS

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The interaction between two closely spaced surfaces, each coated with a liquid film, is important in a broad range of systems, including hard disk drives, microelectromechanical devices, atomic force microscopy, wet granular materials, and capillary condensation in porous materials. For relatively thick liquid films it has been shown that the long-range van der Waals force leads to coalescence of the films at a separation (of order 10^2 nm) which depends on the magnitude of the force and the surface tension of the liquid [1], but which is independent of the film thickness. Very different behaviour is observed in the case of relatively thin films (of thickness of the order of nanometres) [2,3].

Using the surface force apparatus, we have performed a detailed study of the interaction between solid surfaces coated with liquid films, focussing on measurements at small film thicknesses (0–4 nm), the most interesting regime in applications. A jump-to-contact instability occurs at a critical surface separation which increases with film thickness. The dependence of jump-in separation on film thickness is approximately linear, with a slope of 3–4, and we show that this behaviour is consistent with a model of film coalescence induced by van der Waals forces. Our study provides answers to important questions raised in previous work [2,3], and adds significantly to our understanding of the interactions between liquid-coated surfaces.

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PATCHY SURFACTANT COATINGS AND LONG-RANGE FORCES

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One of the most enduring controversies in colloid science is the origin of the so-called "hydrophobic interaction", the anomalous long-ranged attraction measured between hydrophobic surfaces. It has been shown that the electrostatic interaction between surfaces with inhomogeneous charge distributions can lead to an extra attractive force, and this is a possible explanation for at least some manifestations of the hydrophobic interaction. So far, such calculations have only considered surfaces whose charge patches have a fixed size as the separation changes. However, it has been demonstrated that surfactants adsorbed on surfaces can undergo a transition from a uniform monolayer coating to bilayer patches, and that the size and arrangement of these patches can change as the separation changes. We have carried out a complete analysis of the energetics of this transition, and derived criteria for the conditions under which the transition may occur. We find that incomplete ionisation of lipids in adsorbed layers (observed experimentally) may turn out to be a key issue in allowing the monolayer-to-bilayer transition at very low electrolyte concentrations.

PROGRESS IN UNDERSTANDING HYDROPHOBIC INTERACTIONS

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The hydrophobic interaction is among the most important non-specific interactions in biological and many colloidal systems. The significant role of the hydrophobic interaction has led to a great deal of study and yet, over 20 years since the first direct measurement of the attraction between two nominally hydrophobic surfaces, no single theory is able to account for all observed experimental behaviour. One source of confusion in determining the origins of the long-range hydrophobic interaction is the apparent dependence of the attraction on surface preparation technique. As studies of the hydrophobic interaction continue, it becomes increasingly likely that the long-range attraction observed in so many experiments is not in fact due to any direct hydrophobic attraction at all.

In recent years, the combination of atomic force microscopy imaging with surface force apparatus measurements has made it possible to explain the 'long-range' part of this interaction (at separations greater than 200 Å) observed between certain surfaces, though an explanation for the 'short range' part (at separations below 200 Å) remains somewhat more elusive. Direct force measurements between mica surfaces coated in a smooth, stable layer of octadecyltiethoxysilane further supports the idea only the short-range part of the observed attraction between 'hydrophobic' surfaces represents the 'true' hydrophobic interaction.

ANOMALOUS BEHAVIOR IN AQUEOUS THIN LIQUID FILMS IN CONTACT WITH FLUORINATED MATERIALS

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Previous studies have shown that the usual attractive van der Waals force can become repulsive when two dissimilar phases interact through a third phase of intermediate optical properties where one of the surfaces is fluorinated.¹ These studies have been limited to organic thin liquid films. This study investigates the interaction across an aqueous thin film between a fluorocarbon oil droplet and either another oil droplet or a flat solid. This extension to aqueous thin liquid films is made possible by recent advances in the atomic force microscopy (AFM) force measurement technique that has allowed the direct measurement and theoretical interpretation of the interaction between a liquid droplet and a solid surface or two liquid droplets.² Some of our preliminary results (Figure 1) have shown that the interaction between a fluorocarbon droplet and a gold surface was totally repulsive even in high concentration electrolyte solutions. However, the interpretation of this force as a repulsive van der Waals interaction was complicated as results from the interaction between two fluorocarbon droplets appear to suggest an additional non-DLVO force contribution. Further experiments clarifying the short range interactions interpretation for these systems will be presented.

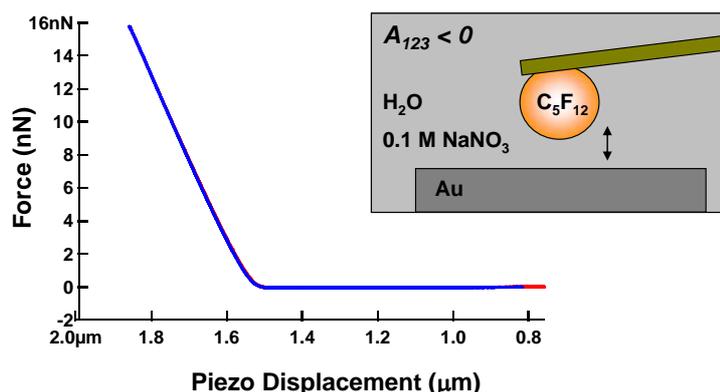


Figure 1. Interaction forces between a fluorocarbon droplet and a gold surface in 0.1 M NaNO₃.

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STATIC AND DYNAMIC INTERACTIONS AT BIOMATERIAL SURFACES

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Surface properties of biomaterials and the way they interact with their environment are investigated in order to control and/or predict biological responses to biomaterials. The areas of biomaterials that will be presented encompass cell surface interactions, drug delivery systems and biolubricating surfaces. Polymers are used to modify and control surface properties such as adhesion, lubricity, colloidal stability and biocompatibility while retaining the key properties of the bulk material. Three topics will be discussed: cell/surface interactions, functionalized liposomes and charged polymer brushes.

Cell/surface interactions are known to induce various responses from cells as apoptosis or active division as well as to affect their rheological properties. Cell/surface interactions and their impact on cell mechanical behavior will be presented. Living cells (rat macrophages RAW 264.7) were seeded on modified mica surfaces at 37.2 °C into a monolayer. Substrates were modified via self-adsorbed or end-grafted polymers. Adhesion and force relaxation of the cell monolayer were investigated using Surface Forces Apparatus. Time dependent deformation and adhesion of interacting adhesive cells for different load-unload velocities and different substrates will be addressed.

Polymer functionalized liposomes exhibiting stealth properties and stimuli-responsiveness have been intensively exploited as drug delivery systems. The behavior of hydrophobically modified pH-sensitive poly(NIPAM) derivatives), undergoing a conformational transition upon change in pH and T, at phospholipid bilayer surfaces was investigated. The influence of copolymer molecular weight, hydrophobic anchor distribution along the macromolecular chain on the stealth properties and stability of the phospholipid membrane will be presented.

End-grafted charged polymers (polymer brushes) are widely used to control and modify surface properties such as adhesion, lubricity and biocompatibility. Correlations between molecular properties of charged brushes (degree of ionization, molecular weight, surface grafting density) and their behaviour (interpenetration and adhesion upon compression, shear response) are investigated. For such correlations to be experimentally established, we developed a methodology to irreversibly attach diblock charged copolymers onto modified mica surfaces with a controlled surface density allowing the end-grafted polymer surface density to remain constant upon changes in environmental conditions (pH, ionic strength, normal load, shearing).

EFFECTS OF CHARGE AND IONIC STRENGTH ON THE ADSORPTION OF LIPIDS ONTO PROTEIN-RESISTANT PEG GRAFT LAYERS

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Non-fouling surfaces are of tremendous interest in a number of areas ranging from biomedical implant devices to the marine industry. Polyethylene glycol (PEG) modified surfaces have proved to be very promising due to their ability to resist non-specific protein adsorption if coated at sufficient density, and to prevent colonization by anchorage-dependent cells. However, although excellent results have been obtained in several laboratories *in vitro*, anecdotal evidence is that PEG coatings have given disappointing *in vivo* performance.

This work addresses the question whether irreversible interactions between PEG coatings and lipids, and perhaps lipoproteins, occur in complex biological media, and whether initial interfacial conversion upon lipid adsorption then causes protein adsorption. We are addressing this issue by adsorption measurements as well as the study of interfacial forces, aiming to gain a molecular physico-chemical understanding of events upon contact. Lipids are an integral part of complex biological fluids and thus revealing their role in biofouling is an important step towards numerous applications.

We have utilized several PEG coatings produced by various grafting routes and have found that their propensity for lipid adsorption varies, and that the nature/charge of the lipid also has a strong effect. The aim now is to attempt to understand the role of PEG grafting density and of the functional polymer underlayer, used to provide the attachment groups for grafting on the interaction, on lipids carrying positive, negative, and no charge, respectively. We use XPS, SPR, and AFM force measurements to gain a molecular understanding of the fouling of PEG modified surfaces by lipids.

Our results demonstrate that some lipids can adsorb onto some protein-repelling “non-fouling” PEG modified surfaces. This shows that before considering any “nonfouling” coating in specific applications one needs to perform comprehensive analysis of how these coatings interact with *all* components of complex biological fluids.

Acknowledgement:

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IMPACT OF SHORT- AND LONG-RANGE FORCES ON PROTEIN CONFORMATION AND ADSORPTION KINETICS

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We have studied the adsorption kinetics of the protein amylase at solid/liquid interfaces. Offering substrates with tailored properties, we are able to identify the individual impact of short- and long-range interactions. By means of a colloidal Monte Carlo approach, the experimentally observed three-step kinetics on specific substrates can be attributed to particle-induced conformational changes of the adsorbed proteins. Our observations show that not only properties of the substrate surface (e.g. hydrophobicity) are relevant, but also van der Waals contributions of the composite substrate, which influence the arrangement of the adsorbed proteins [1]. In this contribution we will concentrate on our newest experimental results involving ellipsometry, scanning probe microscopy and scattering techniques.

[1] A. Quinn, H. Mantz, K. Jacobs, M. Bellion and L. Santen, *submitted*, cond-mat/060717

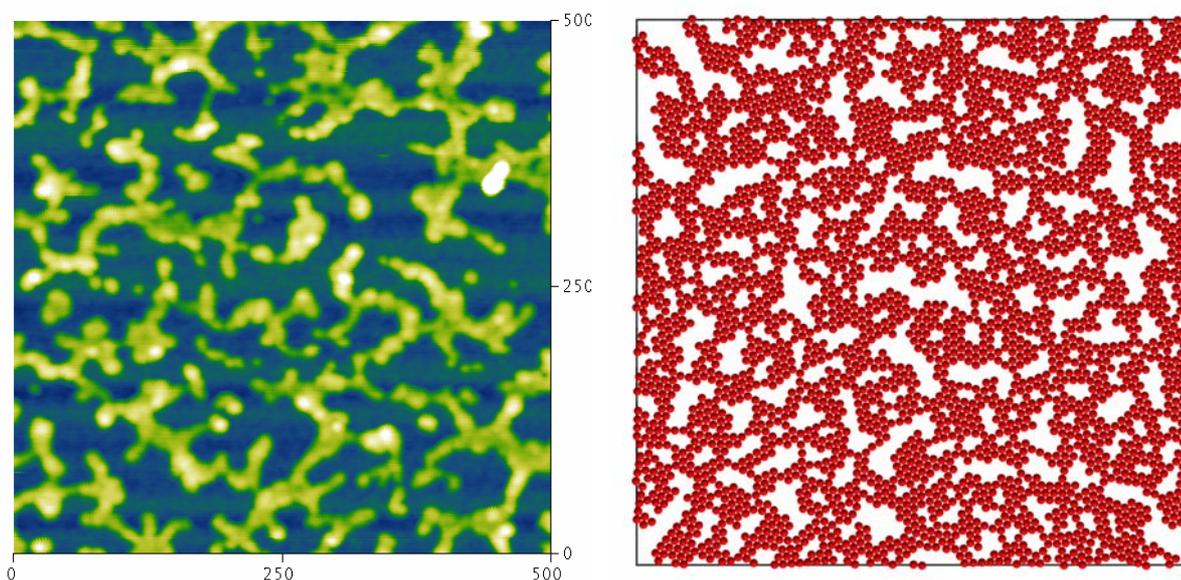


Fig.1 Left: $(500 \text{ nm})^2$ scanning probe microscopy image of amylase adsorbed onto a solid substrate of tailored wettability, height scale 10 nm. Right: Monte Carlo Simulation of a similar model situation.

A NEW ELECTRODE INTERFACE COMPRISING MOLECULAR WIRES AND POLY(ETHYLENE GLYCOL) SPACER UNITS FOR PROBING PROTEIN ELECTROCHEMISTRY

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Understanding and manipulating electronic transfer through molecular-scale “wires” is beginning to attract considerable attention in the developing fields of biosensors and bioelectronics as well as molecular electronics. Molecular wires (MWs) are attractive to bioelectronics is that good electronic coupling over long distance exists between the electron donor at one end and the acceptor at the other. Good electronic coupling is critical for designing an electrode interface for biosensing application so efficient electron transfer between redox proteins and the electrode can proceed. Another important issue for electrode constructs where a molecular wire is integrated with proteins is to ensure the biological molecules interact specifically with the MWs, rather than the rest of the electrode surface. Thus, to achieve a generic surface which ensures specific interactions between a protein and an electrodes requires two important things: 1) molecular wires that can interact directly with the protein and exhibit efficient electron transfer behaviour and 2) diluent molecules that are able to resist non-specific adsorption of proteins.

This presentation is to demonstrate the characterisation and application of a modified electrode interface for protein chemistry. This generic interface is composed of a mixed monolayer of oligo(phenylethynylene) molecular wires and poly(ethylene glycol) (PEG) deposited on glassy carbon electrodes by electrochemically reductive adsorption of the respective aryl diazonium salts. The interface was shown to resist non-specific adsorption of BSA, blood proteins, and HRP using SEM imaging and electrochemistry to the extent. The MWs were shown to allow rapid electron transfer through the PEG diluent layer to a covalently attached ferrocene derivative at rates faster than that previously on glassy carbon electrodes. Covalent attachment of horseradish peroxidase (HRP) to the MWs allowed direct electron transfer to the redox protein with almost ideal electrochemistry, indicating a specific interaction between the MW and HRP, with a rate constant of $13.4 \pm 2.3 \text{ s}^{-1}$. Retained catalytic activity of HRP was demonstrated by the enzyme responding to the addition of the hydrogen peroxide. The rigidity of the MWs, as well as it being longer than the PEG diluent, means this generic interface can be employed to investigate the electrochemistry of a wide range of redox proteins.

FACTORS CONTROLLING THE REACTIVITY OF METAL OXIDE SURFACES

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Metal oxide surfaces are among the most important substrates in the environment as well as in catalytic processes and other areas of modern technology. In an environmental context, they are arguably the most important sorbents for heavy metal and radionuclide pollutants in soils and aquatic systems, with some metal oxides being more reactive than others. The reasons for the observed differences in reactivity, however, are not well understood at a fundamental atomistic level. Key to this understanding is knowledge of surface structural and compositional differences, particularly for hydrated surfaces under ambient conditions. Using $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ as examples, I will present the results of recent *in situ* crystal truncation rod (CTR) x-ray diffraction studies of the hydrated (0001) and (1-102) surfaces of these two isostructural materials, as well as near-ambient x-ray photoelectron spectroscopy studies of their interactions with water and *in situ* x-ray standing wave spectroscopy and grazing incidence x-ray absorption fine structure spectroscopy studies of their interaction with aqueous heavy metal ions. The results of the CTR diffraction studies will be compared with recent density functional and *ab initio* thermodynamic studies of the structure and reactivity of these surfaces.

CHEMICAL SPECIATION, SOLUBILITIES AND SURFACE COMPLEXATION IN Al(HYDR)OXIDE SYSTEMS.

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A detailed understanding of the bioavailability, toxicity, transport and deposition of trace metals and inorganic/organic ligands in natural aquifers requires knowledge of their chemical speciation. Also the optimization of many industrial processes, e.g. within hydrometallurgy, mineral processing and pulp and paper processes relies heavily on the understanding of the chemical speciation in often complicated multicomponent, multiphase systems.

While the importance of solid/solution interfaces is well recognized, the ability to characterize their structure and properties and the processes they mediate is a great scientific challenge. An understanding of interfacial phenomena at the molecular level remains unclear for all but the simplest systems. At the heart of the problem is determination of the surface binding sites and chemical species involved in the interfacial processes. Therefore, ideally, the study of interfacial phenomena must involve measurements that give insight into which species that are present in solution and at the surface. Furthermore, possible dissolution/precipitation processes of the bulk solid phase and surface precipitates must be taken into account.

Recent applications of solution chemistry concepts to describe interactions at the particle - water interface have been very successful. The development of different surface complexation models has implied a better and more detailed understanding of sorption processes at work at hydrous particle surfaces.

Surface complexation has successfully been studied by means of high precision potentiometric titrations combined with appropriate sorption experiments. However, these experimental procedures yield just stoichiometries of the reacting components to form a surface complex and no information on a molecular level. Direct molecular level spectroscopic techniques (e.g. FT-IR, EXAFS, XPS, NMR) are therefore necessary to find out the coordination mode of the metal ion, the ligand and possible metal complexes.

The presentation will focus on the coordination chemistry of Al(hydr)oxide surfaces. Besides their acid/base and surface charge properties, composition, stability and surface coordination features with respect to complexation of organic ligands will be discussed.

TOWARD AN IMPROVED MUSIC MODEL

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Surface complexation models (SCMs) remain the only method to predict surface speciation in the face of changing solution chemistry, but they typically lack meaningful molecular-scale detail. The Multisite Complexation (MUSIC) model of Hiemstra and coworkers is a pioneering attempt to theoretically constrain certain dominant variables (site types and densities, pK_a values) so that meaningful molecular-scale inferences can be made on the basis of SCMs fitted to titration data. However, we have recently shown that the method typically used to predict pK_a values for use in MUSIC models has severe flaws. In contrast, we are developing a new method of pK_a prediction that we hope circumvents these problems.

Any method for predicting pK_a values for use in SCMs must properly separate long-range electrostatic contributions to the reaction energy from more short-range contributions (i.e., a valid “intrinsic” pK_a value must be obtained.) Both the standard MUSIC method and our method use experimental solution monomer pK_a^{int} values to calibrate predictive equations based on bond-valence parameters. However, the standard method (which uses idealized bond-valence parameters as predictors) fails to predict pK_a^{int} values for successive deprotonations of oxyacids (where more and more charge is built up,) so there is no reason to believe it should work for successively deprotonated surfaces. On the other hand, when we use bond-valence parameters derived from *ab initio* molecular dynamics (AIMD) or structure simulations, coupled with Me–O bond ionicity, we are able to predict pK_a^{int} values for successive deprotonations.

Such methods must also adequately account for solvation effects, which dominate acidity. The standard MUSIC method uses fixed numbers of hydrogen bonds with an arbitrarily fixed valence to account for solvation, and derives proton affinity on the basis of the available valence left over on the reacting oxygen atom. However, we have used AIMD simulations of oxo-species in solution to show that there is no leftover valence on these oxygen atoms—the valence sum rule applies here as well as in crystalline structures. Furthermore, we have shown that proton affinity is dependent upon the (quite variable) valence of hydrogen bonds reaching the oxygen atom.

At this point in the development of our method, we are starting to use valence analysis to predict acidity based on AIMD simulations of solvated oxide surfaces. Although this is rather computationally expensive, it can still be accomplished in a reasonable amount of time.

CHARGING BEHAVIOR OF GIBBSITE BASAL (001) SURFACE IN NaCl SOLUTION INVESTIGATED BY AFM COLLOIDAL PROBE TECHNIQUE

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Understanding of surface chemistry of gibbsite $\gamma\text{-Al}(\text{OH})_3$ is essential for controlling the crystallization in aluminium industry and understanding the dissolution and colloidal properties of soil minerals and the related aluminium complex. However, regardless of the increased interest in the surface chemistry of gibbsite, the surface charging behaviour of gibbsite particles in aqueous solution is still not well understood, especially the role that the basal plane plays in the particle's overall proton and charge balance.

We undertook the pH dependent surface force measurements of basal (001) plane of cleaved gibbsite in NaCl solution and show unambiguously that the basal plane of gibbsite develops a net positive charge in the acidic pH range (Y. Gan, G. V. Franks, *Langmuir*, 22 (2006) 6087-6092). Our findings are contrary to the traditional view of surface chemistry of gibbsite that the basal plane is proton inactive in normal pH range. The prevailing empirical multi-site charging model requires modification to take into account the complex surface-solution interaction. This study demonstrates that studying the charging behaviour of atomically smooth surfaces is an essential step towards to a better understanding of the overall charging properties of hydroxides particles.

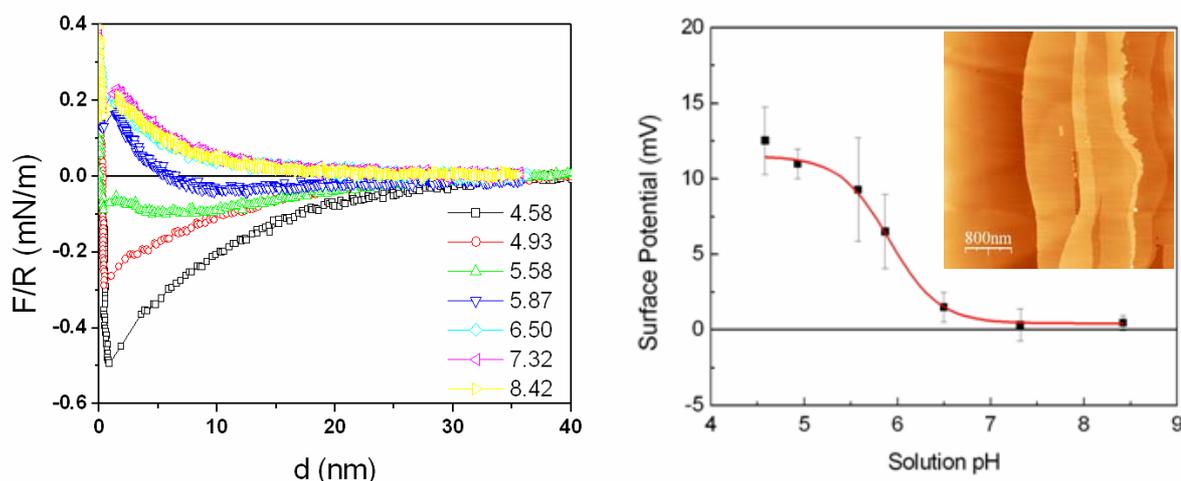


Fig. 1. Left - Force vs. separation distance data for a silica sphere and the gibbsite basal surface in 1mM NaCl at various pH. Right - the best fit surface potentials; the red solid line is the fitting result based on a single- pK_a surface protonation reaction ($\equiv\text{Al}_2\text{OH}_2^+_{(\text{surface})} \Leftrightarrow \equiv\text{Al}_2\text{OH}_{(\text{surface})} + \text{H}^+_{(\text{solution})}$) with $pK_a = 5.9 \pm 0.2$. The inset is an AFM topographical image ($4 \times 4 \mu\text{m}^2$) of gibbsite (001) basal cleavage surface showing steps and smooth terraces.

FREEZE CASTING COLLOIDAL SUSPENSIONS

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Freeze casting is a convenient process of ceramic fabrication where a colloidal suspension of particles is solidified by freezing the liquid medium. If the freezing does not irreversibly destabilize the colloid, the frozen medium can be removed by sublimation in a freeze drying step. Pore-free shaped ceramics can be made by freezing concentrated suspensions. Freezing suspensions containing less than a critical volume powder leads to the formation of particle-free dendrites of the frozen medium. Freeze drying removes the solid in the dendrites, leaving interesting patterns of interconnected porosity. Examples are given for aluminum oxide in water, camphene, naphthalene, and other volatile solids. The size and volume fraction of the dendritic pores are related to the volume fraction powder and solidification rate.

USING TITANIA/SILICA AND TITANIA/ACTIVATED CARBON PHOTOCATALYSTS TO DEGRADE ORGANIC POLLUTANTS AND THEIR REGENERATION

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Volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylenes are emitted from industrial emission and are toxic for humans. They are classified by EPA as hazardous air pollutants. The conventional technologies used to remove VOCs such as incineration, condensation, and adsorption and absorption have the limitation of potentially causing incomplete combustion, and high energy consumption. Photocatalysis is an alternative process to degrade such pollutants. TiO₂ is one of the best semiconductors for photocatalytic oxidation. In this study, three types of titania supported materials including titanium dioxide and silica dioxide composite, titania-coated activated carbon and titania-coated glass beads were prepared and used as photocatalysts in the experiment to remove toluene from the air stream. Their surface areas were analysed. TEM image reveals titania-silica composite were nano-structured aggregates. XRD was used to determine their crystalline phase which was 100% anatase for titania component. A fixed bed reactor was designed and built in the laboratory, the toluene with initial concentration of 300ppm (1149mg/m³) was fed into the reactor, the destruction efficiencies of toluene were determined by the gas analyser. It was also found that TiO₂-SiO₂ aggregates with high surface area (421.1m²/g) achieved high destruction efficiencies. The combined effects of adsorption and photocatalysis were further studied by comparing the performance of pure activated carbon (surface area of 932.4m²/g) and TiO₂ coated activated carbon with BET surface area of 848.4m²/g. It was found that the TiO₂ coated activated carbon demonstrated comparable results to pure activated carbon, and most importantly, the TiO₂ coated activated carbon can be effectively regenerated by UV irradiation, and was reused as adsorbent. The experimental result of titania-coated glass beads demonstrated a steady degradation efficiency of 15% after a period of 17 hours. It helped to understand that photocatalysis degradation ability of the TiO₂ was constant regardless of the adsorption capacity of catalysts. This photocatalytic property can be used to degrade the adsorbed toluene and regenerate the catalyst. This study revealed that if the experiments were designed to use adsorption to remove toluene and followed by regeneration of adsorbent using photocatalysis, it could achieve a very high removal efficiency of toluene and reduce the regeneration cost of saturated adsorbent.

In the second part of this study, TiO₂ was also used for decolouration of high concentration dye effluent. Decolouration rates by the different types of TiO₂ and UV source were determined. The experimental results indicated that dye effluent were degraded efficiently at different levels under the different test conditions including types of TiO₂, UV-A and UV-B light sources. In dyeing process some auxiliary compounds, such as organic acids, fixing agents, surfactants, defoamers, oxidising/reducing agents and diluents, are added in the dyeing solution, which results in the complex composition of the dyeing effluent. These auxiliary compounds have influence on the photocatalytic degradation of dyeing effluent. The dyeing waste water containing 8 different dyes with different auxiliaries has been investigated using TiO₂ pellets as photocatalyst in aqueous solution under UV light irradiation. The influence on photocatalysis process by individual auxiliary compound was investigated in this study.

SYNTHESIS AND ASSEMBLY OF IRON OXIDE NANOCRYSTALS

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Colloidal self-assembly has the potential to offer simple and versatile routes for producing materials or devices for a multitude of functional applications. We have previously studied how spherical silica particles assemble and established the importance of colloidal stability and evaporation rate on the degree of order and defect structure in 2D-arrays. However, in order to go beyond these relatively simple systems, there is a need to integrate various approaches to process and self-assembly particles with the development of a synthetic program to manufacture versatile functional materials.

We will present recent work on the synthesis and assembly of iron oxide nanocrystals. Monodisperse superparamagnetic nanocrystals have been synthesised using the thermal decomposition method of iron soaps in a high-boiling organic solvent. Careful control of temperature and heating rate enabled us to produce monodisperse spheres and cubes at relatively large quantities (figure 1). Evaporation of dilute dispersions on various substrates yields monoparticulate colloidal films and it will be demonstrated how the coverage and short-range order of the deposited nanoparticles can be controlled. The possibility to assemble large-crystals with a pronounced long-range order by introducing weak magnetic fields will also be described and discussed.

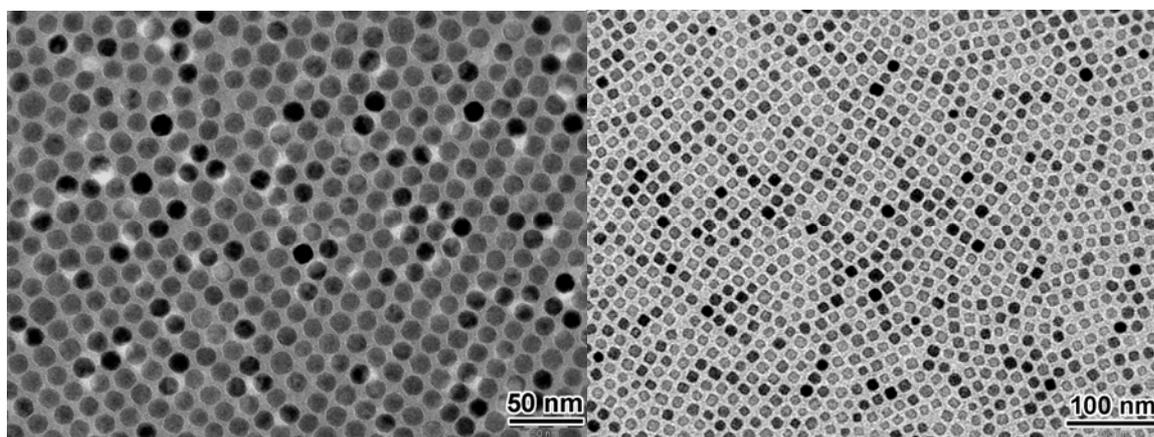


Figure 1: Assemblies of monodisperse iron oxide spheres and cubes

SURFACE CHARGE MODIFICATION OF NANO-SIZED SILICA COLLOIDS

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The surface of commercial 30nm colloidal silica particles was modified by grafting with functional silanes. The high specific surface area and reactivity of the particles due to the small size makes the process susceptible to irreversible aggregation not found previously with larger particles. This study compares surface charge results from different grafting protocols. Measurements of the surface charge and zeta potential as a function of pH combined with X-ray Photoelectron Spectroscopy (XPS) sheds light on the mechanism of instability in nano-sized silica suspensions.

SURFACE MODIFICATION ON SILICONS THROUGH SILICON-OXIDE REACTIONS

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Incorporation of monolayers on silicon surface brings a controlled modification of surface properties standing on the viewpoints of chemically based nanotechnology. Intensive studies of preparation of polymer brushes on silicon surface via controlled or “living” surface-initiated polymerization are also reported. Therefore, to build monolayer and polymer brushes on silicon surfaces, a convenient and wide-usable approach of incorporation of organic moieties on silicon surface is needed. Additionally, flexibility of control and transformation of the attached functional groups on silicon surface is also highly expected.

Here we report novel general approaches of incorporation of organic monolayers on silicon surface. Two reactions of the addition reaction between Si-OH and oxirane ring groups and the condensation reaction between Si-OH and carboxylic acid groups, were applied to silicon surface modification. This approach of modification does not need pretreatment of silicon and reduction of the oxidized silicon (HO-silicon) surface to hydrogen-terminated silicon. Moreover, in the modification reactions only one oxirane group/carboxylic acid group can react with one silanol group without accompanying other side reactions, to make sure the organic moieties incorporated on silicon surface are monolayers. Chemical reactions on the incorporated organic monolayer were performed with functional group transformation and surface-initiated atom transfer radical polymerisation (ATRP). All reactions and chemical structures were examined with X-Ray Photoelectron Spectroscopy (XPS) and atomic force microscopy (AFM).

With the developed methods, design of functional groups and chemical structures as well as control of physicochemical properties of silicon surfaces become easily achievable. This approach is also workable in the modification of glass and ITO surfaces.

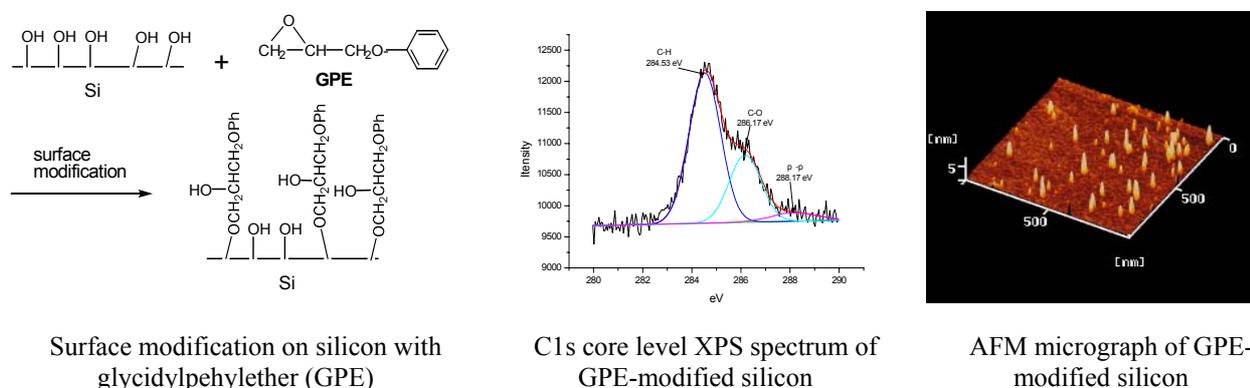


Figure 1. Preparation and characterization of glycidylphenylether modified silicon.

METAL OXIDES IN AQUEOUS PROCESSING SYSTEMS: COLLOIDS, SOLUTIONS, AND SURFACES

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Aqueous processing systems are inherently heterogeneous in nature. Particles, drops, bubbles, films, and bulk phases encounter each other at interfaces. The ability of a reactant or surface-active species to congregate at the interfacial region can, therefore, have crucial consequences on reaction rates, product yields, and product characteristics. In this presentation the critical roles played by the interfacial region and by interfacially active species in materials processing and separations systems are illustrated by considering how: (a) the evolution of silica (SiO_2) nanoparticles in microemulsion-mediated synthesis is affected by surfactant properties and materials synthesis protocols, (b) monodispersed hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles of tuned shapes (e.g., pseudo-cubes, ellipsoids, rods, and “peanuts”) can be synthesized on a large scale from concentrated mixed aqueous solutions containing various additives (e.g., cations, anions, and surfactants), (c) molecular-level modeling of silicon dioxide etching kinetics may be advanced by taking note of the speciation and charge at the silica/aqueous interface, (d) material removal rates during chemical-mechanical polishing of glass can be controlled by surface chemistry through oxide abrasive particle material selection, and (e) aqueous biphasic systems obtained in certain polymer-, surfactant-, and inorganic ion-containing solutions may be utilized (via manipulation of polymer-solid interaction, surfactant adsorption, and electrostatic interaction) to effect liquid-liquid separation of colloidal oxide particles.

BAYER PROCESS SCALE FORMATION

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Scale formation is a universal problem throughout hydrometallurgy. It causes immense costs to society through inefficiencies, lost production, safety issues, costs of additives and plant de-scaling, thereby significantly exacerbating the environmental burden. Historically, efforts to mitigate the problems caused by scale have been derived empirically on a case by case basis within individual industrial operations. It is now generally recognized that there exists considerable scope for improvement, though fundamental understanding is needed for rational advances.

Combined ultrahigh vacuum/electrochemical (UHV-EC) methods were utilized to expose polycrystalline iron and mild steel surfaces to 0.01 M NaOH and for the subsequent transfer back to the UHV analysis chamber without exposure to air. X-ray Photoelectron Spectroscopy (XPS) was then employed to elucidate a chemical description of the iron surfaces as a function of emersion potential. The mild steel electrodes display lower corrosion resistance in alkali solution, underlining a crucial role played by minor alloying components, such as sulphide and/or carbide. Carbonate, an unavoidable contaminant of caustic solutions, is strongly adsorbed to both iron surfaces, its concentration generally being unaffected by a subsequent water wash. Polycrystalline iron emersed in the soluble ferrate domain shows enhanced corrosion resistance, which is suspected to arise through surface impurity enrichment following the anodic leaching of the FeO_4^{2-} species. In contrast, mild steel emersed in the ferrate domain exhibits poor corrosion resistance, further highlighting the detrimental effect of certain alloying elements.

Through electrochemical modification of the iron surfaces, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of the resulting oxide films can be varied consistently between $\sim 1.1 - 0.04$. The interaction of aluminate, carbonate, oxalate, silica and different organics with these surface films is of great industrial relevance, particularly for the Bayer Process, and is currently being studied. The polycrystalline iron and mild steel surfaces are further analysed by Scanning Electron Microscopy (SEM). These UHV-EC experiments offer considerable opportunity to bring substantial benefit to the minerals industry, through gaining a theoretical understanding of the chemistry and physics underlying scale formation on ferrous metals.

FUNDAMENTAL STUDIES OF ALUMINIUM TRI-HYDROXIDE CRYSTALLIZATION FROM SYNTHETIC SUPERSATURATED CAUSTIC ALUMINATE LIQUORS

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Crystallization of coarse aluminium tri-hydroxide ($\text{Al}(\text{OH})_3$) crystals from supersaturated sodium aluminate liquors forms an important step in the Bayer process used in the alumina refining industry for the extraction of alumina from bauxite. Although the Bayer crystallization process was invented over 110 years ago there is still a paucity of fundamental knowledge and understanding of the mechanisms of crystallization process. In the present work, the mechanisms of nucleation and growth of aluminium tri-hydroxide ($\text{Al}(\text{OH})_3$) crystals from optically clear supersaturated caustic aluminate liquors have been investigated to provide fundamental understanding of the inherently slow gibbsite ($\gamma\text{-Al}(\text{OH})_3$) crystal growth kinetics. Numerous *in situ* and *ex situ* techniques including static and dynamic light scattering, cryo-vitrification, cryo-TEM, UV visible spectroscopy, rheology and colloid probe AFM were used to characterize the bulk and interfacial properties and kinetic behaviour of the dilute and concentrated (Bayer liquor type) solutions as a function of supersaturation, ionic strength, temperature and caustic type (NaOH vs KOH) solutions.

Mechanisms for $\text{Al}(\text{OH})_3$ crystallization based upon poly-condensation nucleation and crystal growth theory and underscoring the pivotal role of supersaturation, constitutive and colligative property behaviour of alkali metal ions (Na^+ vs K^+), have been established. The mechanisms of involve initial formation of a loose, Al(III)-containing polymers. Both “monomeric” and “aggregative” growth of the Al(III)- polymers prevail, the latter occurring via the clustering and cross-linking of the polymers to form a network, followed by gradual densification into sub-crystalline (x-ray indifferent) nuclei. Further densification of the nuclei leads to the formation $\text{Al}(\text{OH})_3$ crystallites with still, sub-crystalline diffuse interface. The nature of alkali metal ions (Na^+ vs K^+) in solution plays a key role in the crystallization kinetics, particle size, crystalline phase type (gibbsite vs bayerite) and morphology produced.

INFLUENCE OF DISPERSANT ARCHITECTURE UPON MINERAL OXIDE ADSORPTION

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The dispersion of titania pigments during processing is particularly important in order to prevent the aggregation of pigment particles during the processing and subsequent application of the resulting inorganic coatings. The addition of sodium polyphosphate additives is known to generally aid in the effective dispersion of titania particles during processing. The high temperature and alkaline processing conditions, however, are detrimental to the stability of the sodium polyphosphates which can result in a reduction of the stability of the pigment dispersion.

In this study, the adsorption properties of several mineral oxide suspensions were studied using carboxylate- and phosphate-based dispersants. The adsorption of the polymer dispersants was investigated as a function of acid type, pH and temperature in order to determine the adsorption density and identify the influence of dispersant group composition and structure as a function of oxide type. Adsorption kinetic and isotherm results are correlated with rheological data in order to develop an understanding of the interaction of the dispersing agents with the pigment surface.

ELECTROSPINNING OF CERAMIC OXIDE NANOFIBERS

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Electrospinning and electrospraying are exciting novel approaches to synthesize a variety of nanostructures of ceramic materials, be it nanoparticles, nanotubes, nanofibers, ribbons, or fiber mats. They appear to be amongst the most versatile processing strategies to achieve nanostructures under ambient conditions for many ceramics.

This talk will be present a short overview of the history of electrospinning and recent advances in ceramic nanofiber and nanoparticle synthesis. A novel method for testing the elastic modulus for nanofibers via atomic force microscopy will be discussed. Furthermore, these novel nanomaterials exhibit enhanced or novel properties that allow for potential applications in sensors, filters or high temperature systems.

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THE SINGLE SOURCE CHEMICAL VAPOUR DEPOSITION OF INORGANIC OXIDE THIN FILM SURFACES

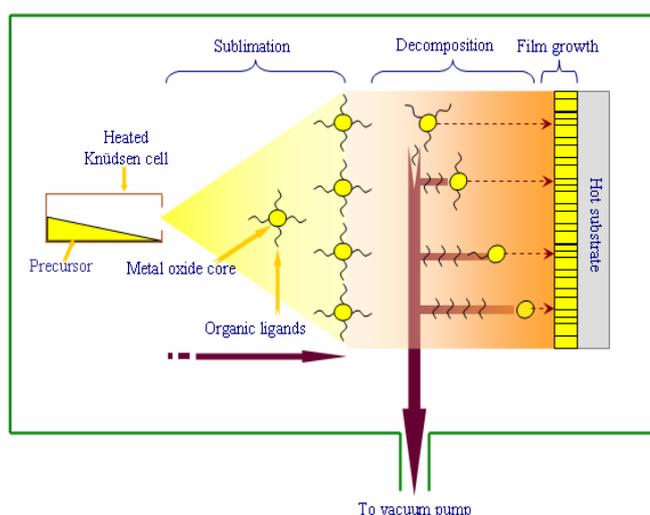
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Metal oxide thin films are dynamic materials that have revolutionised the nature of semiconductor and electronic devices. Recently, progress has stagnated in some aspects due to the increasingly complex deposition apparatus required, and the dearth of suitable precursor complexes of certain ‘difficult’ metals. We present a new pathway to some emerging metal oxide species as well as some classical thin film materials. The use of clever chemistry to simplify otherwise complicated processes has unlocked the potential for new perspectives, and wider applications of metal oxide thin films of the alkaline earth series.

A focus upon the alkaline earth metals has revealed a structure-function relationship between the inorganic oxide precursor material, and the related surface deposited from it. The properties of the resultant surface were able to be manipulated by varying the structural arrangement of the metal oxide sub-units within the precursor molecule. In particular the authors present the results of investigations into materials including MgO, BaTiO₃, and Zn_xMg_{1-x}O, vital for catalysis, computer memory and bandgap engineering. Numerous surface and materials science characterisation techniques were employed to reveal inorganic oxide surfaces in which the stoichiometry, crystallites, and morphology were able to be controlled. The unusual mechanisms for the evolution of these materials have been elucidated, and found to depend strongly upon both the structural arrangement of the inorganic precursor molecule, and the chemistry of the oxide growth interface.



Schematic depicting the growth of the inorganic oxide surfaces.

ROLE OF SPECIFICALLY ADSORBED IONS IN THE LATERAL EPITAXIAL OVERGROWTH OF n-TYPE ZnO IN WATER AT 90°C

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Lateral epitaxial overgrowth (LEO) of ZnO has been demonstrated in water at 90C. The process starts with hydrothermal epitaxial growth of (0001) ZnO on either a (111) spinel substrate or (0001) GaN substrate, followed by Channel Stamping of photoresist to define 'growth windows'. LEO films are then grown in zinc precursor solution at pH 10.9. Addition of sodium citrate controlled out-of-plane growth and enabled the LEO process. Zeta potential measurements show that at the growth pH, negatively charged citrate ions only adsorb on the positive Zn (0001) basal plane of ZnO. TEM studies show a significant reduction in threading dislocations in the wing regions (region that overgrows on top of the photoresist). Micro photoluminescence and Hall effect measurements indicate significant improved material quality. Double LEO demonstrates the possibility of complete dislocation reduction. The talk will emphasize the competitive adsorption of the citrate ions in controlling the growth in the <0001> direction.

TAPPING MODE AFM STUDIES OF POLYMER ADSORPTION ON TALC AND CLINOCHLORE

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Polymers are widely used in industrial applications to modify the properties of bare mineral surfaces. For instance they are used as flocculants¹, dispersants², and depressants^{3,4} in mineral processing. The adsorption of polymers onto layered silicates is of particular interest, as these minerals are responsible for numerous complications in the processing of sulphide ores (hydrophobic gangue flotation, hydrophilic gangue sliming of valuable minerals, etc.). In this study, the adsorption of polysaccharide-based polymers on two types of layered silicate surfaces was characterised using tapping mode atomic force microscopy (AFM). The layered silicates selected were freshly cleaved talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) and clinochlore (chlorite group – $(\text{Mg}, \text{Fe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{O})_8$).

The surface features of the bare substrates in the presence and absence of a number of the polymers were obtained in air and in aqueous solution. Images of adsorbed polymers on the mineral surfaces were obtained at two different initial polymer concentrations (100 and 300 ppm). The images (see Figure 1 for images of one polymer on both surfaces) revealed information on the area fraction of polymer coverage as well as the adsorbed polymer morphology (root mean squared roughness and the apparent layer thickness). The results are discussed in the context of the correlation of the adsorbed layer characteristics with the alteration of the surface properties (e.g. wettability) and the potential binding mechanism of the polymers on the two surfaces.

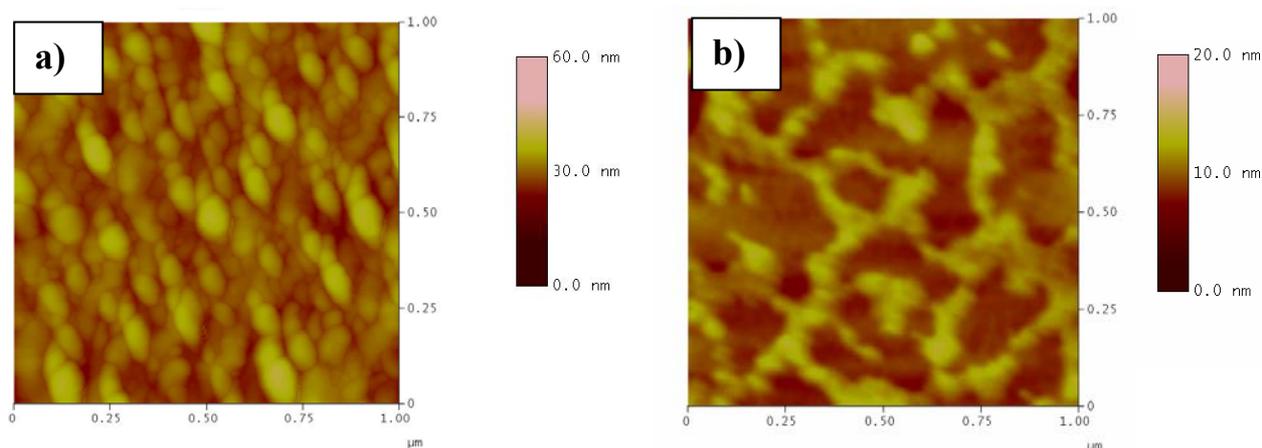


Fig.1. 1x1 μm images of HP Dextrin (100 ppm) adsorbed onto freshly cleaved a) Talc and b) Clinochlore surface in air.

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THE ISOELECTRIC POINTS OF BASAL PLANE SAPPHIRE AND ALPHA ALUMINA POWDER

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The experimentally measured values of the zeta potential and isoelectric points of sapphire (0001) basal plane and submicron alpha alumina powders will be presented and compared. The surface potential of the sapphire crystals was determined by AFM and streaming potential measurements. The zeta potential of both plate-like alumina and equi-axed alumina powders was measured by microelectrophoresis. The results indicate that the iep of the basal plane of sapphire is about 3 to 4 pH units below that typically found for alumina powders. The difference in iep is explained by the hypothesis that different types of surface hydroxyl groups exist on the two different types of surfaces and that these different surface hydroxyl groups have different pK_a values. This hypothesis is consistent with the predictions of multisite complexation modelling and other experiments available in the literature.

FOAMS AND EMULSIONS: THIN LIQUID FILM APPROACH

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Thin liquid films separating bubbles or drops are generally considered to be the key structural elements of foam and emulsion systems containing surfactants, proteins or nanoparticles. At high film thicknesses, film rheological properties, such as film elasticity, impact the foam/emulsion rheological behavior. At low thicknesses (of the order of 100 nm), the interaction forces between surfactant micelles or nanoparticles and the film geometry affect the quality and stability of foams and emulsions. This is especially the case in a concentrated system where micelles or nanoparticles are more likely to come in close contact with one another and become more ordered in the confines of their restricted environment. In recent years, due to the advent of new instrumentation, film rheological properties, as well as surface forces such as repulsive structural barrier arising from micelle/nanoparticle microstructuring, and the attractive depletion force caused by the excluded volume effect, have been characterized. This lecture will highlight the role of film rheological properties and structural forces in stabilizing foams and emulsions. Theoretical results using statistical mechanics are compared with the experimental data.

DEWETTING AND CRYSTALLIZATION IN EMULSION DROPLETS: COLLOID SYNTHESIS AND PURIFICATION

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We have previously shown that rapid dewetting kinetics can occur during emulsion drop crystallization if surfactant interfacial conditions are optimized. The resulting solid morphology is a function of the dewetting and crystallization rate balance, producing solids larger than, similar to, and smaller than the parent droplet depending on that balance.

Here we further examine this phenomenon with an eye toward more fundamental explanation and control of the dewetting effects. The three-dimensional structure of the solids is studied using microscopy and related to the flow patterns experienced during crystallization. Evidence is presented for the ability to align crystallizing lipids at small length scales using the dewetting technique. Quantitative measurements of both the dewetting and crystallization rates are made and related to the oil-crystal contact angle and the oil-water interfacial tension experienced under different surfactant conditions. Comparisons are also made to measurements of the “phase transfer” process used to produce quantum dots via surfactant-induced phase inversion.

Dewetting-enhanced processes are shown to purify the crystallizing material, producing both physical separation of colloids and gradients of molecular weight along the length of the more elongated structures.

INTERFACIAL STRUCTURE AND EMULSION STABILITY OF PROTEIN-CARBOHYDRATE DI-BLOCK COPOLYMERS.

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There is significant interest in the improvement of the emulsification properties of proteins via the conjugation of carbohydrates to proteins. Conjugation of carbohydrates via the Maillard reaction enhances protein emulsion capacity and emulsion stability, an effect that has been related to change in interfacial structure.

This paper examines the structure and emulsion stability of β -lactoglobulin Maillard conjugates. β -lactoglobulin was conjugated to different sized carbohydrates in an attempt to change interfacial thickness. The carbohydrates examined were (a) a series of different molecular weight dextrans and (b) a series of maltodextrins with different dextrose equivalents. The relationships between; polysaccharide molecular weight and interfacial thickness and interfacial thickness and emulsion stability were examined.

The changes in interfacial thickness as measured by latex adsorption were related to emulsion stability. Attachment of carbohydrates to β -lactoglobulin resulted in steric layers of various thicknesses ranging from 0 to 5 nm for the maltodextrin series and 5 to 22 nm for the dextran series. The increase in interfacial layer thickness strongly correlated to the hydrodynamic diameter of the carbohydrate. Increased interfacial layer thickness improved the stability of the emulsion against salt and heat/salt induced flocculation. The results suggest that an increase in layer thickness of 2 nm is sufficient to stabilise these emulsions.

WATER AT HYDROPHOBIC INTERFACES

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Our work on emulsions and other results from the literature indicate that water, and dilute aqueous solutions, spontaneously autolyse with adsorption of hydroxide ions at extended hydrophobic interfaces to create a negative surface charge with the following features:

- the effect is general for unreactive hydrophobic surfaces, whether solid, liquid or gas;
- the observed common isoelectric point about pH 4 implies that hydroxide ion is adsorbed preferentially over the proton by a factor of $\sim 10^6$;
- other anions do not compete with hydroxide at less than 10 mM concentrations; an increase in salt concentration to this level results in typical double layer compression; this implies that dispersion forces are not significant at low electrolyte concentrations;
- the surface charge at the oil/water (O/W) interface is about $5\text{-}7 \mu\text{C cm}^{-2}$;
- most of the surface charge at the O/W interface is compensated by counterion condensation;
- the counterion condensation at the O/W interface is independent of the identity of the cation, from Li^+ to Cs^+ ;
- at the air/water interface there is some cation specificity, with Li^+ reducing the zeta potential more than Cs^+ ;
- the effect accounts for the otherwise unexplained pH dependence of electroosmotic flow in microfluidic channels formed with unreactive polymers;
- the effect implies that the interior of picolitre water droplets in oil will be acidic;
- a molecular interpretation of these effects is obscure, as most theoretical models of water at hydrophobic surfaces have ignored the presence of this intrinsic surface charge;
- a working explanation is that the orientation of water molecular dipoles near the interface creates a large electric field gradient that attracts hydroxide ions and repels protons.

DIRECT MEASUREMENTS OF COLLOIDAL INTERACTIONS AT THE OIL-WATER INTERFACE

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The behavior of particles at fluid interfaces is of great practical interest and importance. The ability of colloidal particles to stabilize two immiscible materials against coalescence was first noted by Pickering, who showed that the stability arose from the attachment of the particles to the oil-water interface. Particulates provide an attractive alternative to surfactant and polymeric stabilizers due to their low cost and relatively benign nature, and are used in applications such as flotation processes, pharmaceuticals and food processing.

Recently, detailed studies of the aggregation kinetics and surface rheology of colloidal particles at the oil-water interface have been reported [1]. In the interest of understanding these macroscopic phenomena from a particle-level basis, we study the interactions between individual polystyrene particles spread at a decane-water interface over a range of length scales, including far-field capillary and electrostatic forces. These interactions are directly measured using time-shared optical traps. A long-range repulsive force is observed with a power-law scaling, in agreement with dipolar interactions mediated by the fractional dissociation of ionizable surface groups [2]. Interestingly, the number of ionized groups inferred from pair interactions is significantly less than the dissociated fraction determined from surface pressure isotherms measured using a Langmuir trough. Furthermore, the particle interactions appear to be highly anisotropic and exhibit multi-body non-additivity. We find that anionic surfactants added to the aqueous sub-phase result in time-dependent interactions, which play an important role in the aggregation kinetics of suspensions. These appear to arise due to decreases in the charge dissociation; possible competing mechanisms, such as changes in the contact angle and surface tension, do not occur. Finally, micromechanical experiments of directly-assembled and naturally formed aggregates provide insight into the near-contact interactions between particles. We observe significant bond rigidity between particles and stick-slip rearrangements, implying that large tangential interactions arise between particles.

In all, these studies provide a new critical link between the nanometer scale interactions that underlie the aggregation kinetics and surface rheology of particulates at fluid interfaces.

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FOAMS DERIVED FROM PARTICLE SUSPENSIONS

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Liquid foams and emulsions are technically and commercially important soft matter. We report about the interfacial criteria of particle stabilized liquid foams. The thermodynamically unstable nature of liquid foams is a critical issue in all applications. Surfactants, biomolecules and colloidal particles have long been known to stabilize oil droplets in Pickering emulsions [1,2]. Partially hydrophobic particles can also attach to gas-liquid interfaces and stabilize air bubbles in surfactant-free diluted suspensions [3,4]. The latter requires an optimum balance between the solid-liquid, solid-gas, and liquid-gas interfacial tensions and the capillary forces in the particle stabilized foam lamella. The stability of such foams is strongly dependent on the wetting behavior of the particle surface. The latter can be controlled by short-chain carboxylic acids, alkyl gallates and alkyl amines. They are appropriate amphiphiles to partially hydrophobize the surface of different inorganic particles in water and oil. For that purpose, the functional groups of the amphiphilic molecule were tailored according to the surface chemistry of the particles.

A simple and versatile method is shown to prepare ultrastable particle-stabilized foams that percolate throughout the entire liquid phase and exhibit no drainage or creaming effects [5]. We describe the foaming behavior of air/suspension systems as well as air/oil/water systems and the properties of the resulting foams including their stability. The universal nature of the method is demonstrated by examples ranging from oxide particles in aqueous media over polymers in apolar media, foamed metal powders, cements and slag components independent of their initial wetting behavior. New application of this method in many different areas is explored now.

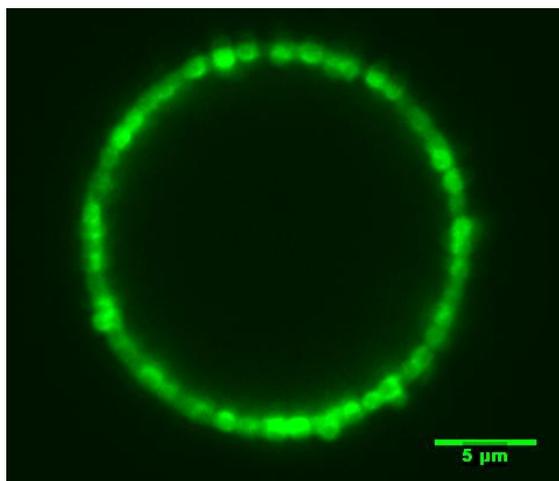


Fig.: Monosized oxide particles stabilizing foam bubble.

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BICONTINUOUS EMULSIONS STABILISED WITH SILICA PARTICLES

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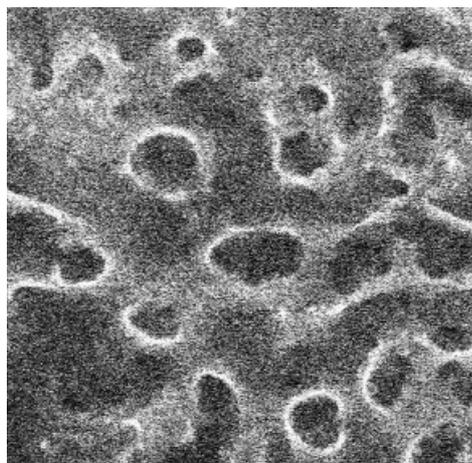
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We present experimental studies of particle stabilized emulsions with bicontinuous fluid domains. In an emulsion two liquids are suspended within each other although they do not mix. To stabilise this out-of-equilibrium situation a third agent is needed. Solid particles with the appropriate wetting properties will lower the free energy of the system dramatically if they sit at the interface between the two liquids. They are permanently trapped at the interface and if jammed against each other form a semi-solid layer. This type of emulsion has been thoroughly studied experimentally.

Exploiting the fact that particles will also collect at the interface when an initially miscible binary liquid system phase separates, we have developed a route to creating novel structures. While conventional emulsions have individual droplets dispersed in the second liquid we like to present an emulsion in the form of a 3-dimensional sponge structure. Adding particles to a system that undergoes spinodal decomposition allows us to 'freeze-in' its typical demixing pattern. This results in a bicontinuous, interconnected system where a particle layer separates the two liquids.

Two miscible liquids will separate in this manner if quenched into the spinodal decomposition region. This can be a temperature quench or pressure quench. While temperature quenches are experimentally more straightforward, pressure quenches are much faster. For most compositions the spinodal decomposition region is separated from the miscible region by a nucleation region which will produce droplets. Therefore temperature quenches can only achieve a limited sample thickness. So far the most successful structures were obtained by quenching through the critical point. Here the nucleation region vanishes and 'critical slowing down' occurs allowing for slower quenches.

Confocal microscopy image (particles = white, liquids= dark) of pattern obtained if silica particles (0.5 μ m diameter) are present during spinodal decomposition. (200 μ m across)



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SILICA NANOPARTICLES; SURFACE CHARACTERIZATION AND FOAMING

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Surface characterization studies were carried out on nine industrially manufactured colloidal silica dispersions (surfactant free, water based, with particles sizes from 5 - 40 nm) and the foam generation (foamability) evaluated in a Bikerman Column. It was established that the foamability was dependent on (a) the particle hydrophobicity (b) the particle concentration (c) the state of agglomeration of the particles. It was found that the foamability varied at natural pH, according to the type of suspension, and the performance could be classified into three groups; high, medium and low foaming. However, for each system, the greatest foamability occurred in the region of the pH_{IEP} (2-3) or the region of highest hydrophobicity and decreased with increase in pH and increase in negative charge. It was also found that the foamability increased with particle concentration (within the 1-15w% solids level). The kinetic viscosity of the concentrated sols (10 w% solids) was found to be very sensitive to the particle size with a drastic increase in viscosity occurring below 7-9 nm. Tests carried out before and after ultrasound treatment indicated that the state of agglomeration of the particle played a role in the foaming performance. These results are discussed in light of recent theories of particle stabilized foam systems.

DYNAMIC FORCES IN EMULSIONS MEASURED WITH AFM

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Much of the ability to produce advanced materials relies on a well developed understanding of surface forces. Static interactions between surfaces have been studied for decades, but a comprehensive quantitative understanding of dynamic interactions in biological or other suspended soft matter systems is still being developed. Dynamic forces can be mediated by a large range of phenomena including adsorption and desorption, surface deformation or hydrodynamic drainage. These effects may be independent or several coupled. The net effect is a dynamic behaviour in the interaction forces in dispersions, emulsions and complex fluids go far beyond the picture developed from existing static theories.

We present a series of examples of how dynamic effects mediate interaction forces for systems with emulsions or soft matter systems. We employed a novel experimental method (1) to study the interaction forces between oil droplets using Atomic Force Microscopy (AFM) and recent theoretical developments (2) to *quantitatively* interpret the experimental results for a variety of systems. These included oil droplets in the presence of an anionic surfactant (3), tri-block copolymers or in the absence of any stabilizers. We find that the colloidal forces, hydrodynamic interactions and surface deformations contribute to the total interaction between droplets. These dynamic forces are the basis behind manipulating and controlling dispersed systems, such as complex fluids or emulsions, in formulation and processing.

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A GENERAL THEORETICAL PERSPECTIVE OF DYNAMICAL INTERACTIONS INVOLVING DROPS AND BUBBLES

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Dynamical interactions involving drops and bubbles are particularly interesting because so many aspects of physics and chemistry are involved. These include colloidal forces, molecular transport within and across interfaces, hydrodynamic of particulate and drop motion, thin film drainage, deformation of interfaces and electrochemical reactions. These phenomena involve large variations in characteristic spatial and time scales that impart further complications. However, such phenomena are key in many manufacturing and industrial operations that range from mineral processing to pharmaceutical, cosmetic and food manufacturing to applications in biotechnology and biomedical science.

Recent progress in experimental investigations of dynamical interactions involving drops and bubbles based on the Atomic Force Microscope and the Surface Force Apparatus and video imaging will be considered in parallel with theoretical developments in understanding such experiments. General paradigms and results that are useful in analysing dynamical interactions involving such systems will be presented. Such results may have broader implications in helping to resolve issues such as hydrodynamic boundary conditions that may be applicable on the nano scale and the determination of key instrumental parameters such as the spring constant in Atomic Force Microscope cantilevers.

DETERMINATION OF FORCES BETWEEN EMULSION DROPS IN WATER-IN-OIL EMULSION BY NEUTRON SCATTERING AND OPTICAL INTERFEROMETRY

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The forces between emulsion drops in water-in-tetradecane emulsions were investigated by Small-angle neutron scattering (SANS) and optical interferometry. Crude emulsions were prepared by sonicating the mixture of tetradecane (continuous phase), aqueous ferrofluid (dispersed phase) and emulsifier (span 80). A monodisperse emulsion was obtained by fractionating the crude emulsion in an electromagnet. Monodispersity of the emulsion was confirmed by neutron scattering which gave the diameter of the drops as 172 ± 4 nm, in good agreement with that determined from dynamic light scattering. Two dimensional detector images of the scattering patterns clearly revealed chains of emulsion drops aligned along the external magnetic field lines, with no evidence for the droplet deformation. Chain structure is obtained by modeling the SANS patterns. Force versus separation curves from SANS and optical interferometry agreed within experimental limitations, showing hard-core interactions between span 80-coated water droplets.

EFFECT OF HYDROPHOBICITY AND SURFACE CHARGE ON WETTING AND TIME-SCALE OF ATTACHMENT OF BUBBLES TO SOLIDS

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Bubble collision with solids and formation of the three phase contact (gas/liquid/solid), TPC, is a necessary condition for attachment of the bubble to a hydrophobic solid. For the bubble attachment the following processes need to proceed: i) thinning of the intervening liquid film between the bubble and solid, ii) rupture of the liquid film (when the critical rupture thickness is reached) and formation of a “hole” of the TPC, and iii) expansion of the “hole” and formation of the three phase contact perimeter (area) assuring stability of the attachment. It has been rather common understanding that if the solid surface is highly hydrophobic (contact angle $\theta > 90^\circ$) then every collision should result in the bubble attachment. However, we demonstrated recently that even in the case of such a model hydrophobic surface as Teflon, the colliding bubble could bounce a few times without attachment, both in water and surfactant solutions. Experimental data acquired recently indicate that gas presence at hydrophobic solid surface is of crucial importance for the bubble attachment.

Further experiments were conducted with mica surfaces modified by electrically driven deposition of the polyelectrolytes PDADMAC (poly(diallylmethyl-ammonium chloride)) and PSS (poly-4-styrene sulfonate) to give positively or negatively charged surfaces respectively. Contact angle values in water determined by drop shape analysis for PDADMAC and PSS terminated surfaces were found to be similar (30-40°). Kinetics of the three phase contact formation and attachment of the colliding bubble to the modified mica surfaces in solutions of the cationic surfactant DTABr were monitored using a high speed camera (1182 Hz). Results of the kinetics of the attachment were compared to static contact angle measurements. Our data indicate that formation of three phase contact (TPC) and the bubble attachment to modified mica surface is influenced to a significant degree by surface charge. This is consistent with observations made in a modified surface force apparatus of repulsive interactions between untreated mica having a negative charge and a low water contact angle, and a bubble carrying a weak negative charge.

Acknowledgement:

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SPECIFIC ION EFFECTS ON BUBBLE COALESCENCE INHIBITION IN MIXED ELECTROLYTE SYSTEMS

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Ion specificity is at the heart of many biological processes and is important in all soft matter systems at high electrolyte concentrations. The effect of electrolytes on bubble coalescence in water is a simple example of ion-specificity. Single electrolytes inhibit coalescence or have no effect, as predicted by ion combining rules based on empirical assignments (α or β)^{1,2}. The mechanism behind electrolyte inhibition, as well as the salt differentiation, is not understood. We here report that mixed electrolytes also follow the ion assignments. In addition, inhibition is consistent with the hypothesis that electrolyte effects depend upon ion separation within the interfacial region and offers support for a recent suggestion by Marčelja³ regarding the origin of the combining rules. We demonstrate that Gibbs elasticity is not the mechanism by which coalescence is inhibited; rather we propose that some electrolyte combinations modify the hydrodynamic boundary condition at the air-water interface resulting in the manifestation of ion-specificity at long-range even at high electrolyte concentrations.

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SUPRAMOLECULAR INTERFACIAL ARCHITECTURES FOR OPTICAL BIOSENSING

Wolfgang Knoll

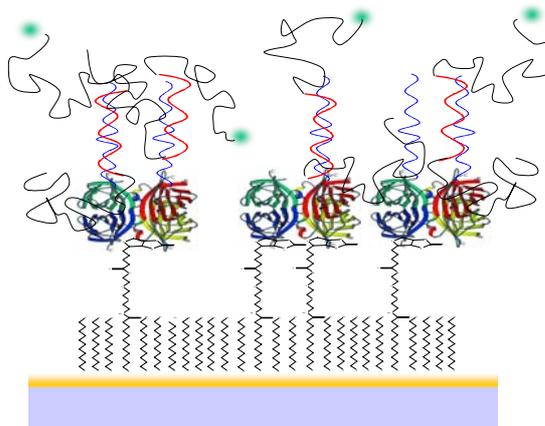
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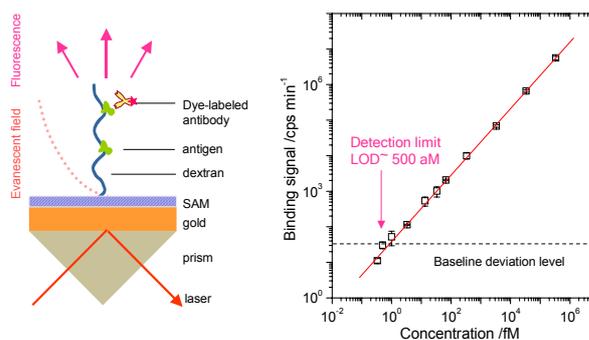
This report summarizes some of our recent efforts in developing biosensor platforms based on surface plasmon optics. We will focus mainly on two different aspects. The first one concerns the implementation of surface plasmon diffraction as a novel label-free detection principle with significant advantages over the classical reflectivity scan in normal SPR.

The second mode of operation combines the field-enhancements achievable at resonant excitation of surface plasmon waves with fluorescence detection principles. We will demonstrate that with this technique unprecedented sensitivities in DNA diagnostics and in protein affinity studies can be reached.

The interfacial sensor architecture for PCR Amplicon detection



Extremely sensitive biosensor by surface plasmon fluorescence spectroscopy (SPFS)



MICROGEL PARTICLES: AN OVERVIEW

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This lecture will present an overview of recent studies of microgel dispersions and of monolayers of microgel particles deposited on surfaces. Microgel particles are particles of cross-linked polymers, copolymers or polyelectrolytes, dispersed in a solvent medium, which swell (with solvent) and deswell in response to changes in the local thermodynamic conditions. Triggers for such a response include temperature, solvent composition and light, and in addition, for polyelectrolyte-based systems, pH and ionic strength. In this lecture several types of microgel system will be discussed, including those based on poly(N-alkylacrylamides), poly(vinyl pyridine), and amphoteric systems. Both equilibrium swelling and swelling/deswelling kinetics will be discussed.

Microgel particles provide interesting systems for the study of controlled aggregation and rheologically-responsive dispersions, and for controlled uptake / release. With respect to the latter topic, an overview will be presented in regard to the uptake and release of polymers, surfactants and nanoparticles, with potential applications in a wide range of technologies, from drug delivery to the controlled release of bactericides, perfumes and flavours.

HIGH THROUGHPUT APPROACHES TO POLYMER FORMULATION

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Commercially available combinatorial and high throughput fluid handling and measurement capabilities have enabled tremendous progress in industrial product development; however, the platforms are often costly and time-consuming to implement. The approach adopted by most manufacturers has been to build automated platforms that mimic the development process for a specific material in a narrow application. This greatly increases data acquisition rates, but it is challenging to adapt this system-specific infrastructure to changing research needs. In response, our research aims to develop new methods for the manipulation and measurement of complex polymeric fluids, thereby providing flexible and inexpensive alternatives to robotics driven instrumentation.

To improve the versatility of high throughput formulations testing, we employ microfluidic technology to build a toolset of complementary library fabrication and test methods. The preparation of devices is fast and modular, allowing for rapid prototype development and increased flexibility. Our fabrication method is an adaptation of existing procedures that uses an optical resin with good solvent resistance that obeys a frontal polymerization mechanism, which enables us to prepare quasi-three-dimensional channel structures.

We have demonstrated the use of microfluidic chips for the synthesis, mixing and measurements of a variety of systems. Synthetic techniques include controlled radical polymerization on a chip (CRP chip), and organic phase droplets as polymerization microreactors. Microarray libraries have been produced from sequences of droplets with varying co-monomer compositions. Measurements and methods include polymer shrinkage, interfacial tension, on-line fiber-optic Raman spectroscopy, and static and dynamic light scattering. These new approaches enable rapid, often real-time, evaluation of solution properties as composition is systematically varied. The methods have been applied to challenges in dental composite formulation, a variety of 2-phase fluids, and surfactant solutions.

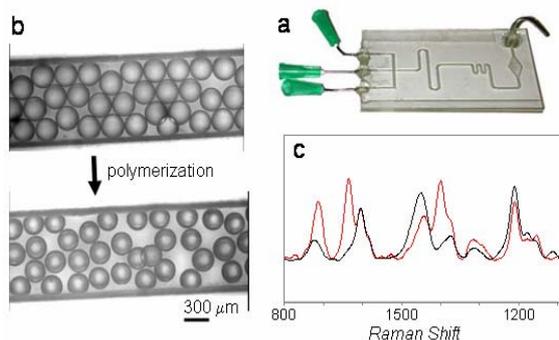


Figure 1: a.) A thiolene microfluidic device used to create, mix, polymerize and characterize monomer droplets. b.) Optical images of monomer droplets and polymer particles. c.) Raman spectra of monomer (red) and polymer (red).

IN SITU POLYMERIZATION AND SELF-ASSEMBLY OF CATIONIC SURFACTANTS

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Polymerization of self-assembled amphiphiles with preservation of nanostructure is a goal that is not commonly achieved. Often the properties of the monomer and various oligomers produced as reaction proceeds are so dramatically different that the polymerized structure is unrecognisable from its starting point. Successful control over self-assembly as the structure evolves from dynamic equilibrium into a permanently-rendered state with polymerization offers a novel route to the preparation of hierarchically structured, functional and novel composite materials.

In this work we will describe a base-catalysed ionic polymerisation of derivatives of cationic, N-alkylpyridinium surfactants that may be carried out in polar or aqueous solutions. The reaction may be started and stopped at will by addition of base or acid, so that equilibrium oligomer distributions can be isolated and the characterised. Characterization of the micelles and lyotropic phases formed by the monomer and oligomer mixtures by optical microscopy and small-angle x-ray scattering will be described. We will also report on the *in situ* polymerization and controlled reorganization of a micellar solution of monomer into a dispersion of polymerized hexosomes. Using real-time kinetic small-angle neutron scattering together with SAXS and electron microscopy characterization of the nanostructured dispersion, we will demonstrate how the size of the hexosomes can be controlled by acid-quenching.

PROTON CONDUCTIVE COMPOSITE MEMBRANE OF PHOSPHOSILICATE AND POLYVINYL ALCOHOL

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Proton conductive composite membranes were prepared by dispersing phosphosilicate colloidal particles into a polyvinyl alcohol (PVA) matrix. The synthesized membranes were flexible with film thickness between 80-200 μm . SEM micrographs show that the phosphosilicate particles are homogeneously dispersed, whilst the PVA crosslinks with the inorganic phase and fills in the gaps between the particles. Proton conductivity increased by several orders of magnitude with increasing humidity, reaching a maximum of 0.02 S/cm at ambient temperature and 100% relative humidity (RH). The activation energy reduced to 7.3 kJ/mol with RH increasing to 90% in the tested temperature range 20-70 $^{\circ}\text{C}$. On the basis of the structural characterization and conductivity measurements, proton transport is deemed to occur by both the Grotthuss and diffusion mechanisms. The methanol permeability was found 5-10 times lower than Nafion 117. The composite membrane was tested in the direct methanol fuel cell (DMFC). The preliminary results show the membrane is a promising candidate for PEM in DMFC systems.

STRUCTURAL BEHAVIOUR OF THERMORESPONSIVE POLYMER-GRAFTED SURFACE IN AQUEOUS SOLUTIONS

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It is well known that poly(N-isopropylacrylamide) (PNIPA) exhibits thermally responsive properties in aqueous solutions. In water, PNIPA has a lower critical solution temperature (LCST) at around 32°C and PNIPA chains show a phase transition from a coil to globule state. When PNIPA chains are immobilized onto solid surface, they are expected to show similar structural change on the surface responding to temperature. Such structural behaviours may have a number of interesting applications where a responsive character triggered by temperature is important including drug delivery, permeation-controlled filters and controlled/sustained release. Therefore, in order to control the structure of such layers three-dimensionally, it is important to investigate in detail the structural behaviour of immobilized PNIPA chains responding to stimuli from external environment.

In this study, structural changes of PNIPA chains immobilized on solid surfaces were investigated in aqueous solutions with an atomic force microscope (AFM) and a quartz crystal microbalance with dissipation (QCM-D). A PNIPAAm layer was grafted on silicon wafer surface by free radical polymerization of NIPA. By AFM imaging, the transition of the grafted PNIPA chains from brush to mushroom state was clearly visualized; the surface images of the plate were featureless at temperatures below the LCST, whereas a large number of hemi-spherical structures whose size was order of 100nm were found on the surface above the LCST. Both frequency and dissipation signals obtained using QCM-D showed significant change at around LCST, indicating that PNIPA underwent a collapse by the dehydration of the chains.

A complementary investigation indicated that a similar transition could be observed in solutions of high concentration electrolytes. It was also found that the size of the mushroom structure of PNIPA chains after transition was altered by the concentration of the electrolyte solutions.

STRUCTURE OF LIQUID CRYSTALLINE NANOSTRUCTURED DRUG DELIVERY PARTICLES BY SYNCHROTRON DSC-SAXS

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Whilst lamellar liquid crystalline particles (liposomes) have been used for some time in pharmaceutical and cosmetic products, the potential application of non-lamellar liquid crystalline particles, such as Cubosomes, Hexosomes and Spongosomes, is yet to be exploited, principally due to a lack of fundamental understanding of their nanostructure and how to utilize the differences in structure to obtain a commercial or therapeutic outcome. An understanding of the impact of manufacturing and in use conditions for these nanostructured materials is also lacking.

In these studies we have used SAXS and synchrotron DSC/SAXS to further investigate the influence of temperature and additives on the nanostructure present in the bulk and particulate forms of a matrix of liquid crystalline materials, varying in both the chemical composition (phytantriol, glycerate, and glyceryl monooleate-based particles), the phase structures targeted (reverse cubic phases and hexagonal phase), and heating/cooling cycles ranging from 1 to 10 °C/min. Interestingly, substantial supercooling effects are observed on cooling these systems from reverse micellar phase – up to 30 °C supercooling is often required to induce transition to the equilibrium phase structure. In some instances the phase progression on cooling also differs from that observed on the heating cycle. One particular example of such behaviour are phytantriol-based submicron-sized cubosomes, for which a bicontinuous cubic to reverse micellar phase transition occurs directly on heating at approximately 70°C, but does not transform from the reverse micellar phase to cubic at all, and requires cooling to 45°C before transformation to a reverse hexagonal phase, with a bicontinuous cubic phase reappearing below 40°C. The behaviour is reproducible for the same sample and also occurs at different heating rates.

These results contrast those of previous reports that LC particles are in effective thermodynamic equilibrium on heating and cooling. As heat homogenization is often employed as a means for preparation of these particles, these results have important implications for both their manufacture and for understanding and optimizing drug release from these particles.

REVERSIBLE DNA LINKAGES IN MODEL, MULTIPARTICLE THERAPEUTIC ASSEMBLIES

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An ideal therapeutic vehicle often involves delivery of multiple therapeutic and diagnostic agents. The tunable affinity and reversible association between complementary oligonucleotide strands makes DNA a remarkable materials assembly tool; however, past investigations have focused on reversing association between complementary surfaces via thermal denaturation of DNA linkages. Here, our goal is to expand the use of DNA linkages to model, multiparticle therapeutic assemblies in which competitive hybridization is employed at a fixed temperature to release particles from the assembly following delivery. DNA hybridization between immobilized probe sequences and primary target sequences first drives the assembly of complementary particle surfaces. A longer, secondary target sequence is then added to displace the primary target strand and effectively melt the DNA linkages between the surfaces and break up the assembly. Flow cytometry results indicate that only a four-base difference in the longer, secondary sequence is needed to drive the competitive displacement of soluble primary target strands. Fluorescence and confocal microscopy studies of colloidal assemblies indicate that reducing the number of DNA linkages formed between immobilized probe and primary target sequences favors faster subsequent particle disassembly via competitive displacement.

DYNAMICS OF STRUCTURAL TRANSFORMATIONS BETWEEN LAMELLAR AND INVERSE BICONTINUOUS CUBIC LYOTROPIC MESOPHASES

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Lyotropic liquid crystalline phases, displaying differing degrees of dimensionality, form when amphiphilic molecules are mixed with a polar solvent. These phases include the fluid lamellar (L_{α} ; 1-D), hexagonal (H_I/H_{II} ; 2-D) and inverse bicontinuous cubic phases (Q_{II}^P , Q_{II}^D , Q_{II}^G ; 3-D). All of these structures are based upon lipid bilayers, the basic building blocks of biological membranes. The complex phase behaviour and energetics of such self-assembled systems have received a great deal of attention over the past half-century and the gross outline of this field is well understood. Nevertheless the out-of-equilibrium behaviour of lyotropic systems is not well explored.

The fluid lamellar to inverse bicontinuous cubic phase transition is believed to proceed via stalk-like intermediates in a process which is structurally similar to the mechanism by which biological membranes fuse. The process of membrane fusion underlies a vast array of fundamental biological processes such as endo- and exocytosis, fertilization and enveloped virus infection and the Stalk Mechanism of membrane fusion has received considerable theoretical attention. Analysis of membrane fusion using biological membranes is difficult due to the complexity of the system and model systems are increasingly used to identify and understand such processes. An increased knowledge of such lyotropic transformations in lipid systems will therefore be of central importance to our understanding of endo- and exocytosis and to the design of lipid packaging for the effective delivery and translocation of DNA in gene therapy.

The fluid lamellar (L_{α}) to double-diamond inverse bicontinuous cubic (Q_{II}^D) phase transition for the amphiphile monoelaidin in excess water has been studied by means of both temperature and pressure jumps. Pressure-jump experiments were carried out at the ID02 beamline of the European Synchrotron Radiation Facility, Grenoble (France) using a high pressure x-ray sample cell capable of altering hydrostatic pressure within 7ms. The transition exhibits a remarkable sequence of structural transformations. Our data imply that the transition dynamics depends on a coupling between changes in molecular shape and the geometrical and topological constraints of domain size. We propose a qualitative model for this coupling based on theories of membrane fusion via stalks and existing knowledge of the structure and energetics of bicontinuous cubic phases.

FORMATION OF AMPHIPHILE SELF ASSEMBLY PHASES IN PROTIC IONIC LIQUIDS

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Numerous studies have been carried out on lyotropic systems of amphiphiles in water. However, surfactant aggregation in polar non-aqueous systems has been less extensively investigated and has typically involved solvents such as amides, glycols and alcohols. One exception to these is ethylammonium nitrate (EAN) which is a protic ionic liquid (PIL). Until recently however, there have been few reports of this new class of self assembly media.

In this work, a range of protic ionic liquids have been identified as capable of supporting the self assembly of non-ionic surfactants such as myverol and phytantriol, as well as of the cationic surfactant hexadecyltrimethylammoniumbromide (CTAB). PILs-surfactant penetration scans and light polarising microscopy have been used to observe the liquid crystalline phases formed. Lamellar, inverse hexagonal and bicontinuous cubic phases have been observed and may exist in thermodynamic equilibrium in excess PILs. Variation of the cation and anion within the PIL can be used to modify the lyotropic behaviour. Further, PILs that possess higher cohesion energy, contained hydroxyl functionalities and had short alkyl chains supported a greater wealth of mesophases and further, increased the thermal stability of these phases.

SURFACTANT DISSOLUTION: KINETICS AND EQUILIBRIA OF RHEOLOGICAL VARIATIONS

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Liquid surfactant consumer products are increasingly concentrated as a result of consumer trends and the increasing cost of petroleum-based solvents. Because concentrated surfactants often exhibit liquid crystalline phases, their dilution and dissolution are often rate-limiting steps in product processing and usage. Previous work has shown the importance of modeling the formation rate of various equilibrium liquid crystalline phases but has not focused on structural variations and their contribution to dissolution kinetics.

Microscopic observations are made of water diffusion into aqueous liquid crystalline surfactant solutions during dilution. The rate of diffusion is measured relative to the rate of dissolution using polarized light microscopy to track the different interfaces formed as the system progresses from lamellar, to cubic, to hexagonal, to micellar phases. In addition to tracking equilibrium phase transitions, structural transitions from wormlike to spherical micelles are visualized using local measurements of rheology with position. As composition changes during dilution rheology also varies over an extremely wide range as a result of the different microstructures that occur, leading to remarkable spatial gradients in modulus.

Here we calculate and measure the additional diffusion resistance presented by various micelle structural variations under static and convective boundary conditions. Dynamic measurements are made of sharp rheological gradients using a novel imaging technique.

Keynote Lecture

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{ABSTRACT NOT RECEIVED}

DESIGNING NANO-STRUCTURED POROUS MONOLITHS

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Porous nano-structured materials have attracted a wealth of interdependent scientific research due to their commercial and potential uses in fields as diverse as catalysis, separation and chromatography. Pore engineering of such materials together with a versatile ease of introducing functionality allows for specific applications to be targeted.

Microporous (< 2 nm) aluminosilicates such as zeolites excel at shape selective sieving but are not effective in affecting transformations of foreign species which are too large to access the internal surface. Mesoporous (2 – 50 nm) solids answered this requirement to allow for immobilisation of larger biological molecules such as proteins and inorganic nanoparticles. Macroporous (> 50 nm) solids allow for low pressure drops and high flow rates. Tailoring the pore size and connectivity over a wide range of length scales in a monolith has potential to deliver optimum performance.

Fine-tuning materials with porosity on a hierarchical length scale have attracted attention as the synergistic effect of multimodal pores is expected to be superior over the individual monomodal species for tailored applications. However, preparing well-defined monoliths with defined hierarchical porosity in a rapid and facile manner with significant mechanical strength of an arbitrary shape remains a challenge.

Here we report a novel and facile approach for the rapid fabrication of mechanically stable hierarchical nano-structured monoliths of arbitrary shape by partial fusion of a powder body of nanoporous particles. Subjecting the powder body simultaneously to a compressive stress and rapid heating results in surface deformation and necking of particles at the surface to form a continuous body. Control over the physical properties (e.g. pore volume, pore size, surface area and mechanical strength) within the monolith is demonstrated as a function of the forces applied during the processing technique.

SYNTHESIS OF SILICA HOLLOW MICROSPHERES WITH MESOPOROUS SHELL STRUCTURE VIA COLLOIDAL TEMPLATING

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This research synthesized hollow silica microspheres via a sol-gel coating technique together with organic particles acting as a sacrificial template. Precursor molecules (TEOS) were first adsorbed on the template surface to form a core-shell composite structure before being subjected to thermal pyrolysis for the removal of organic core. Both the precursor formulation (including the relative concentration of TEOS, water and ethanol) and process parameter were varied, and their effects to the morphology and structural configuration of the hollow spheres were examined by FTIR, BET, FE-SEM, TEM, XRD, TG/DTA and dynamic light-scattering particle size analyser.

The synthesized hollow spheres are amorphous in structure. Particle size of the synthesized hollow spheres is about 1 μm from SEM and TEM observations. Increasing the reaction temperature appears to facilitate the formation of hollow spheres. In particular, the hollow silica spheres always form when the reaction temperature is held at 50 - 60 $^{\circ}\text{C}$ and the water concentration is under 4 moles. A "phase diagram" for the hollow silica formation is also established. The residual inorganic weight is found to increase with the reaction temperature. The outer particle size decreases with the increasing ethanol concentration, while the BET surface area reduces when the concentration of water is increased. Shell structure of the hollow microspheres is mesoporous; to which, pore size measured from the as-synthesized particles is about 2.7 - 4 nm and this becomes slightly smaller to about 3 - 5 nm after thermal pyrolysis.

INKJET-PRINTED GOLD NANOPARTICLE FILMS FOR CHEMICAL SENSORS

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The electrical conductivity of gold nanoparticle/organic hybrid materials is extremely sensitive to changes in nanoparticle core-core separation [1]. As a result of this sensitivity, such materials can be exploited as sensing elements for the detection of volatile organic compounds in so-called “electronic noses” [2, 3]. The incorporation of organic vapours into the gold nanoparticle/organic film results in an expansion of the film, thereby increasing the electrical resistance. By tailoring the surface properties of the nanoparticle with different thiol ligands, the selectivity towards various analytes can be readily tuned.

Inkjet printing is an attractive technique for controlled deposition of small quantities of material [4]. Recent years have seen inkjet printing technology become a fast-growing tool for the fabrication of organic transistors, light-emitting diodes, ceramics and biopolymer arrays. One major challenge is the reliable preparation of thin films, as this requires suitable control of the ink viscosity, surface tension and evaporation of the solvent. The properties of inkjet printed gold nanoparticle films and their application as a chemiresistor device will be presented.

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REVES MOLECULAIRES EN OXYGENE ET CARBONE

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For some 15 years the attainment of efficient, non-fluorinated CO₂-active surfactants has been a “Holy Grail” for researchers spanning pure and applied chemical sciences. This talk outlines the history of small molecule CO₂-active surfactants, from the first tentative observations with fluorinated compounds in 1991, up to recently discovered fluorine-free oxygenated amphiphiles.

Reference

Surfactants for CO₂

Julian Eastoe, Sarah Gold, David C Steytler, *Langmuir* **2006**, *22*, 9823-9842.



SURFACE INTERACTIONS WITH BIOMACROMOLECULAR SURFACES DERIVED FROM WOOD

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The recent literature has shown that the preparation and use of model wood biopolymer surfaces has proven to be a popular research front. Numerous techniques have been described for the preparation of these thin films using a variety of raw materials resulting in model surfaces which can be used in subsequent measurements of fundamental surface interactions with relevance to pulp and paper chemistry. These model surfaces aim to reduce the experimental variability caused by the inherent differences in the natural fibre systems and to create a surface with a well defined structure and surface chemistry. However, the model cellulose or lignin thin film is ultimately influenced by the preparation procedure with differences in both the surface chemical species and crystallinity resultant. Thus careful consideration needs to be given to how well the model surface relates to the real fibre system.

In this presentation, the use of crystalline and amorphous cellulose model substrates for the study of surface chemistry and interactions important to many processes in the pulp and paper industries will be discussed. The benefits and disadvantages of three preparation procedures will be shown with particular attention paid to surface forces measurements undertaken in an aqueous environment. These measurements have allowed the determination not only of the Hamaker constant for cellulose, but also the surface potential as a function of ionic strength at relatively low electrolyte concentrations. Furthermore, the use of different model cellulose surfaces in adhesion measurements along with a study into polymer and polyelectrolyte adsorption will be discussed.

In many circumstances, the surface chemistry of wood fibres can be considered to be lignin-rich. This is especially true for fibres liberated through mechanical pulping mechanisms or kraft pulping where lignin may be precipitated onto the fibre surface in the latter stages of the cook. In this study, the adsorption of polyelectrolytes to stable, continuous, model lignin films will be discussed. A range of strong and weak polyelectrolytes were used with other variables including the solution pH and ionic strength. The adsorbed amount and kinetics of adsorption were measured with both optical reflectometry as well as through using the quartz crystal microbalance (QCM). QCM measurements also allow the determination of the visco-elastic properties of the adsorbed polyelectrolyte layer which leads to an understanding of the extension of the polyelectrolyte molecules away from the interface. This extension is thought to highly influence bonding between fibres and also retention of filler particles.

PATTERN FORMATION ON TILTED SUBSTRATES BY COLLOIDAL SELF-ASSEMBLY USING FLOW-CONTROLLED VERTICAL DEPOSITION METHOD

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Self-assembly method has been successfully explored to fabricate three-dimensional (3D) colloidal crystals as well as 2D monolayer and surface patterning. Among many techniques developed for fabricating the colloidal assemblies, vertical deposition (VD) is proven to be one of the most effective methods, which provides a good control over the thickness and morphology of the colloidal assembly.

In this research, the revised VD method, flow-controlled vertical deposition (FCVD) method, was applied to fabricate the colloidal films. By manipulating the tilting angles of the substrate, α , and the suspension flow velocity, i.e., the velocity of the dropping liquid surface, U , as well as the particles size, D , various morphologies including distinctive striping patterns of the colloidal films have been formed. The relationship between the structures of the colloidal films and the tilting angles together with the dropping velocity of the liquid surface was clarified. A phase diagram is established for pattern formation as a function of α , U , and D . The derived knowledge will be useful in clarifying the mechanisms involved in the formation of colloidal crystals/films.

POLYPHILE AND MIKTO-ARM SELF-ASSEMBLY: POSSIBLE MESOSTRUCTURES

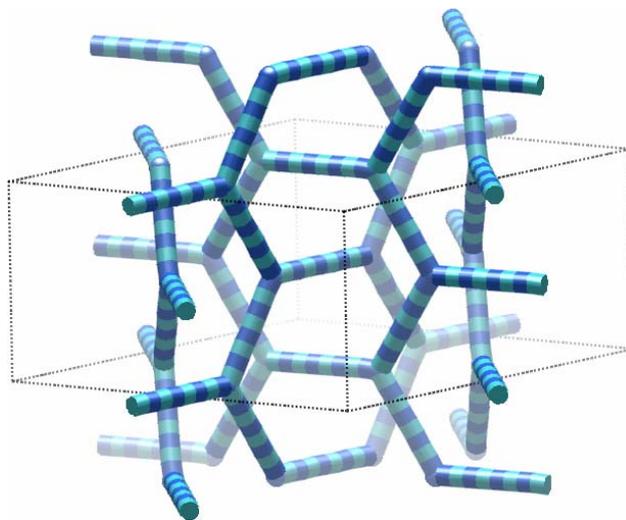
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Amphiphiles are a special class of molecules containing two immiscible domains – hydrophobic and hydrophilic -- allowing self-assemblies to be analysed in terms of 2D interfaces separating those domains. Polyphiles are molecular analogues with more than two mutually immiscible domains and all domains sharing a common junction in the molecule, of similar architecture to so-called mikto-arm copolymers. The molecular architecture of polyphiles imposes complex topological constraints on polyphile self-assemblies. For example, they form interfaces separating domain pairs, pinned to junction lines common to all the interfaces.

We have derived a variety of possible mesostructures for polyphiles containing 3 domains and find a number of curious geometries, including tricontinuous interwoven 3D domains, interwoven 2D domains and combinations of 1D, 2D and 3D domains. For example, 3 interwoven graphite arrays (shown below), which we can think of as 3 obliquely oriented smectic mesh stacks, satisfy the topological constraints.



The relationship between these mesostructures and local molecular shape suggests a first-order (at this stage purely geometric) theory of such self-assemblies, that involves interfacial curvatures and line curvature, related to the molecular chirality and splay.

THE ISOELECTRIC POINT/POINT-OF ZERO-CHARGE OF INTERFACES FORMED BY AQUEOUS SOLUTIONS AND NON-POLAR SOLIDS, LIQUIDS AND GASES

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From our previous work on the role of the electrostatic field strength in controlling the pH of the isoelectric point (iep)/zero-point-of-charge (pzc) of polar solids we have extended the analysis to predict that the pH of the iep/pzc of a non-polar solid, liquid or gas-aqueous interface should occur at $\text{pH } 1.0 \pm 0.5$. Consideration of a wide range of experimental results covering non-polar solids such as molybdenite, stibnite, sulphur or paraffin as well as hydrocarbon liquids such as xylene, decalin and long chain ($>C_8$) alkane oils, as well as nitrogen and hydrogen gases, all in various simple 1:1 electrolyte solutions, confirm the general validity of the result. We further consider various models of water structure at non-polar material-water interfaces in relation to the origin of the charge on and electrical double layer properties of non-polar material-water interfaces.

PHASE BEHAVIOUR AND MICROSTRUCTURE OF MICROEMULSIONS WITH A ROOM TEMPERATURE IONIC LIQUID AS THE POLAR PHASE

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Microemulsions of non-ionic alkyl oligoethyleneoxide (C_iE_j) surfactants, alkanes and ethylammonium nitrate (EAN), a room temperature ionic liquid, have been prepared and characterised. Studies of phase behaviour reveal that EAN microemulsions have many features in common with corresponding aqueous systems, the primary difference being that higher surfactant concentrations and longer surfactant tailgroups are required to offset the decreased solvophobicity the surfactant molecules in EAN compared with water. The response of the EAN microemulsions to variation in the length of the alkane, surfactant headgroup and surfactant tailgroup has been found to correspond to that observed in aqueous systems in most instances. Small Angle Neutron Scattering (SANS) reveals a single broad scattering peak for the microemulsion phase, as per aqueous systems. This data was modelled using the Teubner Strey model. A lamellar peak was also observed for surfactants with longer tailgroups at reduced temperatures. Phase behaviour, SANS and conductivity experiments have allowed the weakly to strongly structured transition to be identified for EAN systems.

THE INFLUENCE OF A ZWITTERIONIC POLYMER ON THE STABILITY OF COLLOIDAL DISPERSIONS AND SURFACE PROPERTIES

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Concentrated dispersions find applications in many industrial systems such as paints, paper coatings, detergents, ceramics, and pharmaceutical formulation. The understanding of interparticle interactions is essential to control the stability/flocculation of these dispersions. The most effective procedure for the stabilisation of dispersions is to use a surface-active polymer, which strongly adsorbs on the surface of the particles and can be applied in the presence of high electrolyte. Polymeric material can be specifically designed to have a strong 'anchor' chain and a 'stabilising' chain that extends from the surface leading to strong repulsion between particles approaching each other.

This study examined the adsorption of a zwitterionic polymer onto silica particles and its effect on the stability/flocculation of varied concentrated dispersions. The adsorption of polymer onto plane surfaces was previously established in our research group using AFM, ellipsometry and neutron reflectivity as a function of ionic strength and polymer concentration.

We find that the polymer adsorbs strongly to silica particles and leads to bridging flocculation or steric stabilisation depending on the polymer concentration. The viscoelastic properties of these suspensions were investigated using shear stress - shear rate and oscillatory rheological experiments, as a function of ionic strength, volume fraction of silica particles and order of mixing.

These zwitterionic polymer results will be used as a model for more complex artificial proteins and their effect on the stability of colloidal dispersions.

ULTRASOUND INITIATED MINIEMULSION POLYMERIZATION OF METHACRYLATE MONOMERS

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When sound waves pass through a liquid medium, cavitation, referring to the growth and violent collapse of microbubbles, can be induced. The cavitation process promotes a wide range of chemical reactions, such as the synthesis of polymers and the production of metal nanoparticles. By sonicating a mixture of organic monomer and water to create an emulsion, polymer latex particles in the size range of about 100 nm can be produced¹. The sonochemical polymerization process is initiated by the reaction of primary radicals (H• and OH•) with free monomer molecules. The physical effects from the collapse of microbubbles, specifically the shear forces generated during the bubble collapse, are responsible for the narrow size of the polymer particles produced. The ultrasound initiated emulsion polymerization of methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and 2-ethylhexyl methacrylate (2EHMA) in the presence of sodium dodecylsulfate as a stabiliser produced latex particles in the size range of 70 nm to 110 nm with molecular weights of the order of $2-6 \times 10^6 \text{ g mol}^{-1}$. The experimental data obtained show significant differences in the rates of polymerization of the methacrylate monomers in the order 2EHMA > BMA > MMA. The rate trend can be partly explained with respect to the physicochemical properties of the monomers. It is suggested from the results obtained that the mechanism involved in sonochemical formation of the latex particles is very similar to that of a conventional miniemulsion polymerization process.

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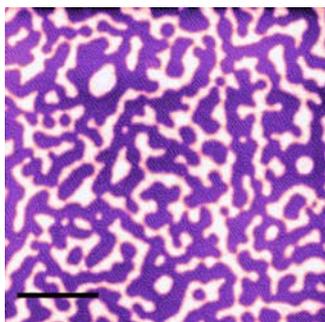
MICROPATTERNING OF PROTEINS: A NEW APPROACH USING THIN POLYMER FILMS

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The ability to control protein and cell positioning on a microscopic scale is crucial in many biomedical and bioengineering applications, such as tissue engineering and the development of biosensors. We propose here a novel, simple, and versatile method for the micropatterning of proteins. Micropatterned substrates are produced either by the dewetting of a metastable polymer film on top of another polymer film or by the micro-phase separation of block-copolymers. Selective adsorption, or micropatterning, of proteins can be achieved on such substrates by choosing pairs of polymers which differ in protein affinity. Fluorescence microscopy and atomic force microscopy (AFM) provide evidence that model proteins adsorb preferentially on isolated bio-adhesive micropatches in a protein-resistant matrix. "Inverse" protein patterns, containing non-adhesive islands in a protein-adhesive matrix can also be produced. Such micropatterned substrates could potentially be used in the development of biosensors and bioassays, and in the study of cell growth and motility.



AFM image of a block copolymer thin film annealed in order to induce microphase separation of the blocks. Scale bar 10 μm .

INVESTIGATING THE MECHANISMS OF PROTEIN RESISTANCE IN OLIGO ETHYLENE GLYCOL-LIKE PLASMA POLYMER FILMS THROUGH NEUTRON AND X-RAY REFLECTOMETRY

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Non-fouling protein repellent surfaces are a subject of great interest within the academic and industrial communities. The performance of many biomedical, biosensor and drug delivery based devices is critically dependant on their protein resistant properties. One of the most common of all surface coatings employed to render a surface non-fouling is through the use of poly(ethylene glycol) (PEG). PEG polymers are amphiphilic, they form directional bonds with water, adopt high order intrachain structure and exhibit complex phase behaviour. Although PEG coatings are widely used to prevent or reduce protein adsorption, the mechanism of the protein repellent properties is an area of ongoing contention. ‘Steric repulsion’ and the effect of the ‘water barrier’ from the structure of water in the near environment of the PEG chains are the two most common theories described in the literature.

In this study we have used the technique of radio frequency glow discharge plasma polymerisation to investigate low-fouling films produced by diethylene glycol dimethyl ether (DG) on a heptylamine (HA) plasma polymer (pp) primer layer. The interaction of water with DGpp films was investigated using a number of techniques including Neutron and X-Ray reflectivity, X-ray Photoelectron Spectroscopy (XPS), Contact angle goniometry, Electrokinetic Streaming Potential Measurements, and AFM.

We have found that surface free energy and potential is not a key determinant in the protein resistance of inert DGpp films nor is the hydrophilicity and roughness of the films. We believe the key factor in determining the protein resistance of a very thin hydrated DGpp displaying an extremely short range steric repulsive interaction is the retention of a high density of residual ether functionality.

IN-SITU OBSERVATIONS OF ADSORBED MICROGEL PARTICLES

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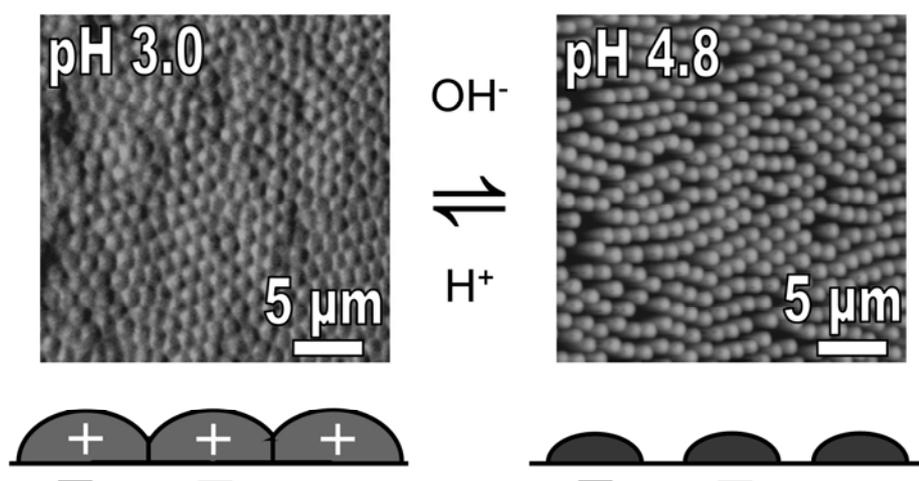
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Microgels are lightly cross-linked colloidal particles that can exist in two states: a non-solvated latex form and a swollen gel form when exposed to a stimulus, such as a change in pH, or a temperature trigger. Usually, this volume transition is reversible for non-interacting particles in dilute solution. The behaviour of various types of stimulus-responsive microgels has been studied extensively in bulk solution. In view of the many potential applications for ‘smart’ surfaces, such as functional coatings for controlled uptake and release, micro-optics, and stimulus-responsive membranes, recent research has turned to microgel activity at interfaces.

The formation and morphological changes of a pH-responsive microgel layer on silica and mica were studied by *in situ* Tapping Mode Atomic Force Microscopy, and on silica using optical reflectometry (O.R.). First, lightly cross-linked, sterically-stabilised poly(2-vinylpyridine) (P2VP) particles were adsorbed in their non-solvated latex form at pH 4.8 to produce a structurally-disordered monolayer that covers the entire substrate. Addition of acid to this particulate film induces a latex-to-microgel transition at pH 3.0, causes particle swelling (and also some desorption) and produces a uniform, swollen film with localised hexagonal packing. Returning to pH 4.8 causes partial microgel deswelling to form individual P2VP latex particles, which retain the localised order previously induced by swelling. The swelling and collapse of this P2VP film was reversible during subsequent pH cycles, with no further desorption observed. The adsorbed amount of P2VP latex/microgel was quantified at each pH by determining the surface density and dimensions of the adsorbed particles. These measurements allow a microgel surface excess to be calculated for the first time.



DIRECT NUMERICAL SIMULATIONS OF ELECTROPHORESIS OF CHARGED COLLOIDS

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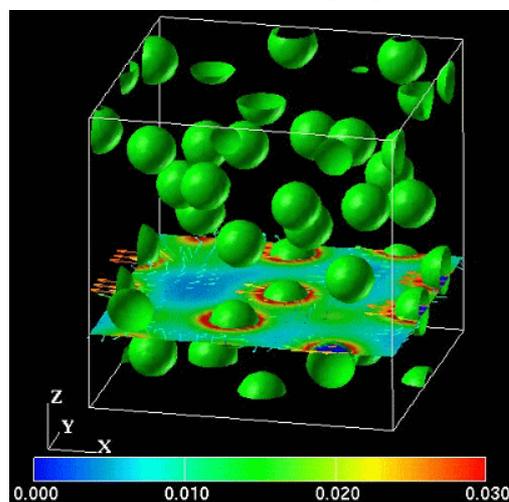
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Electrohydrodynamic phenomena are of great importance in physical, chemical, and biological science, and also in several engineering fields. In the case of electrophoresis of charged particles for example, the particles start to move on the application of external electric fields. The electric double layer around charged particles tends to be deformed and its distribution becomes anisotropic because of the applied external field and also of the friction between ions and fluids. In this situation, the time evolutions of the colloidal particles, the ions, and the host fluids are described by coupled equations of hydrodynamics (Navier-Stokes) and electrostatics (Poisson) with proper boundary conditions imposed on the surfaces of the colloidal particles. However, the usual numerical techniques of partial differential equations are hopeless to deal with dynamical evolutions of many-particle systems since the moving particle-fluid boundary condition must be treated at every discrete time step.

Recently, we have proposed a reliable and efficient numerical method, called smoothed profile (SP) method, to resolve the hydrodynamic interactions acting on solid particles immersed in Newtonian host fluids. In the SP method, the original sharp boundaries between colloids and host fluids are replaced with diffuse interfaces with finite thickness. This simple modification greatly improves the performance of numerical computations since it enables us to use the fixed Cartesian grid even for the problems with moving boundary conditions. The SP method is not only applicable to the dispersions in Newtonian fluids, but also particularly suitable for the particle dispersions in complex fluids for example electrolyte solutions. Field-particle hybrid simulations were performed; where the density of ions was treated as coarse-grained continuum object while colloids were treated explicitly as particles. The interaction between fields and particles were taken through the diffuse interface. The purpose of the present study is to establish an efficient and reliable simulation method applicable for electrohydrodynamic phenomena such as electrophoresis.

In the presentation, we briefly outline our numerical modelling for charged colloidal dispersions and then demonstrate the reliability of the combined SP method by comparing our numerical results with classical theories such as O'Brien-White theory. Finally, comparisons are made for the electrophoretic mobility of dense dispersions, where the simulation results show notable deviations from a mean-field type theory according to the cell model.



THE PHASE DIAGRAM OF A MIXED ANIONIC/CATIONIC SURFACTANT SYSTEM: TRANSITION FROM MICROSTRUCTURE TO NANOSTRUCTURE

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The phase behavior and aggregate structures of mixtures of the oppositely charged surfactants cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) are explored at high dilution by pulsed field gradient stimulated echo (PFG-STE) NMR. The aggregation numbers and hydrodynamic radii of vesicles and mixed micelles were determined by a combination of viscosity and self-diffusion coefficient measurements. The average size of the mixed micelles was larger than that of micelles containing uniformly charged head groups. Analysis of the variations of the self-diffusion coefficient and viscosity with changing concentration of CTAB or SDS in the cationic-rich and anionic-rich regions revealed a phase transition from vesicles (microstructure) to mixed micelles (nanostructure). Differences in the lengths of the CTAB and SDS hydrophobic chains stabilize vesicles relative to other microstructures (e.g., liquid crystalline and precipitate phase), and vesicles form spontaneously over a wide range of compositions in both cationic-rich and anionic-rich solutions. The results obtained from viscosity measurements confirmed this transition. In addition, by experimentally measuring the diffusion coefficient and viscosity, we determined the aggregation number and the outer and inner radii of the vesicles as a function of solution composition and total surfactant concentration.

Previously, we used molecular thermodynamic theory to examine mixed ionic and nonionic surfactant systems. In particular, we found that by using this theory, we could explain the experimentally observed behavior in terms of the free energy contributions to mixed micelle formation.

In the present study, a capacitor model was developed for estimating the surface potentials and electrostatic free energy (g_{elec}) in vesicles.

Keywords: Phase behavior; pulsed field gradient spin-echo NMR; microstructures; nanostructure; liquid crystalline; vesicles; cationic-rich; anionic-rich; capacitor model.

VISCOELASTIC MICELLAR SOLUTIONS IN NONIONIC FLUORINATED SURFACTANT SYSTEMS

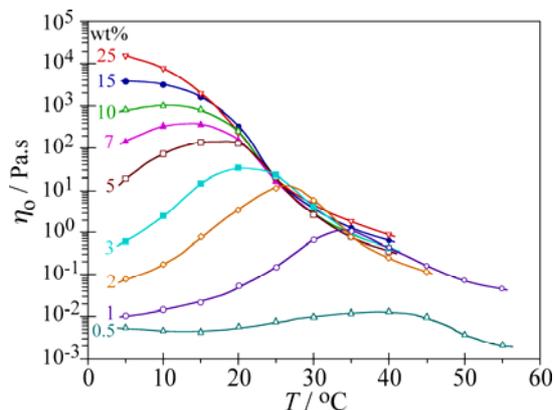
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Formation and rheological behavior of viscoelastic wormlike micellar solution in aqueous solutions of nonionic surfactant system, perfluoroalkyl sulfonamide ethoxylate $C_8F_{17}SO_2N(C_3H_7)(C_2H_4O)_nH$ (abbreviated as $C_8F_{17}EO_n$), has been studied. In water- $C_8F_{17}EO_{10}$ binary system, a temperature induced viscosity growth takes place, which is evident even at a low (~ 1 wt%) surfactant concentration. Wormlike micelles undergo one-dimensional micellar growth with increasing temperature and the viscosity increases swiftly to reach its peak at a temperature $T_{\eta\text{-max}}$, where a viscoelastic solution of micellar network is formed. With further increase in temperature, the network density increases but the viscosity decreases swiftly due to formation of micellar joints and ultimately a phase separation occurs. In consistence with the rheological results, evolution of small angle X-ray scattering patterns provide direct evidence of temperature-induced micellar growth and the structural change at high temperatures. Upon increasing surfactant concentration, the extent of micellar growth increases and viscosity increases sharply at low temperatures. Hence, the $T_{\eta\text{-max}}$ corresponding to viscosity-peak shifts toward low value with increasing surfactant concentration.



Zero shear viscosity (η_0) – Temperature plots for $C_8F_{17}EO_n$ –water system at various surfactant concentrations.

A more hydrophilic surfactant, $C_8F_{17}EO_{20}$, forms a low-viscosity micellar solution in surfactant-water binary system, but a viscoelastic micellar solution is formed up on adding a hydrophobic surfactant, $C_8F_{17}EO_3$. Up on successive addition of $C_8F_{17}EO_3$, viscosity decreases sharply and a phase separation takes place. The effect of the concentrations of each of the surfactants and temperature on the rheological properties and micellar growth in the mixed system will be discussed.

ADHESION TO WET CELLULOSE – DESIGN RULES FOR POLYMERS, PEPTIDES AND PROTEINS

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Over the last decade our laboratory has investigated agents giving adhesion to wet cellulose, a slightly anionic and very hydrophilic surface which is very resistant to adhesion. Although a wide variety of cationic water soluble polymers and biomacromolecules will adsorb onto wet cellulose, adsorption is not synonymous with adhesion strength. For example, poly(diallyldimethyl ammonium bromide), PDADMAC, a common industrial water soluble cationic polymer readily adsorbs yet gives poor adhesion. In general, electrostatic effects are not very important for wet adhesion.

Joints formed with wet adhesives can be divided into three classes – Heat-cured, Damp-dried and Instantaneous Joints. Heat-cured Joints must be dried and cured at high temperature to form a water resistant joint. Examples include many proteins, which crosslink at high temperature, and reactive synthetic polymers such as dextran aldehyde.

Damp-dried Joints must be dried at least at ambient temperature to give a water resistant joint. Polyvinylamine, polylysine and lysine rich proteins fall into this class. Whether or not covalent bonds form in Damp-dried joints is an open question.

Instantaneous Joints form in water when the adhesive can form strong bonds, either covalent or physical, in water. The only example we have found of an Instantaneous adhesive is phenylboronic acid derivatives of polyvinylamine which form esters with some carbohydrates in water. Two reports in the literature suggest that polymers modified with cellulose binding module proteins may also give instantaneous wet joints.

MANIPULATION OF WETTING MORPHOLOGIES ON TOPOGRAPHIC SUBSTRATES

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In microfluidic applications rapid and efficient handling of small amounts of liquids is a crucial requirement. Here, we study open microfluidics on topographically structured substrate, which contain free liquid/vapor (or liquid/liquid) interfaces. Liquid deposited on grooves with rectangular and triangular cross section, has a variety of possible morphologies determined by the contact angle of the drop on the planar substrate and the aspect ratio of the groove (*i.e.* ratio of depth to width of the groove or opening angle). Hence, in order to obtain a certain liquid morphology, one must match surface topography and wettability by a careful choice of geometry and wettability. Filling and drainage behavior of these grooves were studied as function of time and contact angle.

In our experiments, electrowetting is used to tune the contact angle of the liquid reversibly from about 95 to 50 degrees, leading to a reversible transition between a droplet morphology at large contact angles and extended liquid filaments for small contact angles. The transition is capillarity-driven but the behavior of the liquid above the transition is influenced by the electrical properties of the liquid. The length of the liquid filament is a function of the applied voltage and can be explained by a simple electrical model. This gives us a precise handle to manipulate liquid on-demand in open microfluidic micro grooves. In contrast to grooves with rectangular cross section, the liquid filaments in triangular grooves undergo a spinodal instability when being quenched from a filling to a non-filling situation. The liquid filament breaks up into regularly spaced droplets with a preferred distance.

SIMULTANEOUS DETERMINATION OF QUASI-STATIC AND DYNAMIC FORCES USING MAGNETICALLY ACTIVATED COLLOID PROBE FREQUENCY MODULATION AFM

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The study of fluids in confined geometries has been of great interest in recent times with applications in the understanding of the properties of microfluidic devices and colloidal dispersions alike. The nature of these hydrodynamic interactions in industrially relevant dispersions, which are often highly concentrated, heated and / or sheared, dominates the interaction potential and thus determines the stability of such systems. It is the study of these systems which deviate from the dilute, quasi-static nature of interactions described by DLVO theory alone that has driven instrument development in the pursuit of measurements of the traditional quasi-static interactions and the hydrodynamic interactions both *simultaneously* and *independently* in both SFA¹ and AFM^{2,3} communities. These sub-resonance surface modulation techniques have been limited in excitation frequency by inertia and often require extensive characterisation to eliminate an instrumental influence upon the detected phase and amplitude response.

Frequency modulation AFM (FM-AFM) utilises a phase locked loop to feedback upon changes in resonant frequency of a driven cantilever due to tip-sample interactions. This ensures that the system is always driven at resonance. In constant amplitude FM-AFM, a second feedback loop controls the excitation amplitude. The driving voltage output from this loop is a direct measure of the dissipative component of the tip-sample interaction. The use of these independent feedback loops allows the quantitative separation of the conservative (quasi-static) and dissipative (hydrodynamic) forces from a single measurement. Magnetic activation is achieved by attaching a magnetic particle (NdFeB) to the backside of the cantilever and imposing a modulated magnetic field. This direct activation of the cantilever removes the ‘forest of peaks’ normally associated with piezo activation in liquid environments and simplifies the system since only the tip of the cantilever is driven.

The application of FM-AFM to colloid probe measurements has allowed the limitation of previous studies to be addressed. In addition to the technical aspects of the measurement, data will be presented outlining the ability of this novel technique to quantitatively elucidate both the quasi-static forces described by DLVO and the hydrodynamic interactions both *simultaneously* and *independently*. The true resonant nature of the measurement allows access to velocities approximating those of concentrated dispersions undergoing Brownian motion without impacting upon the quasi-static forces normally obtained using static colloid probe measurements.

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CATASTROPHIC PHASE INVERSION OF TOLUENE-DILUTED HEAVY OIL EMULSIONS IN ELECTROLYTES BY ROTOR-STATOR. PART 1. SIZE, ELECTROPHORETIC MOBILITY AND SPECIFIC CONDUCTIVITY

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The occurrence of mixtures of oil-in-water (O/W) and water-in-oil (W/O) in the same process streams during heavy oil extractions warranted further investigations into the conditions under which phase inversion occurs during high shear mixing. Catastrophic phase inversion (PI) of several heavy oil concentrations in toluene for varied diluted oil fractions in model process water (*mpH₂O*) and in NaCl electrolytes at basic pH was investigated. Emulsions were created after high shear turbulent mixing by a rotor-stator. The inversion fractions were detected by abrupt changes in not only electrophoretic mobility and zeta potential decrease, but also in decreased specific conductivity and pH, and increased droplet size. Results showed that phase inversion occurred at different inversion fractions of oil for *mpH₂O* (0.70) and NaCl (0.50 to 0.6). All data were consistent for the PI fractions of oil. The emulsions were less stable in NaCl than in *mpH₂O*.

Key words: heavy oil emulsions, catastrophic, phase inversion, electrolytes, electrophoretic mobility, rotor stator, turbulent mixing, droplet size.

INTERFACIAL PROPERTIES OF ROOM TEMPERATURE IONIC LIQUIDS

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Organic salts with melting points in the vicinity of room temperature (or below about 100 °C) are commonly designated as ionic liquids (IL). These liquids have unique physico-chemical characteristics: no significant vapour pressure, non-flammability, good thermal stability and a wide useable temperature range. There is a large (and rapidly growing) interest in their use as clean solvents in organic synthesis, catalysis, extraction, etc. ILs are highly concentrated electrolytes and have potentially important electrochemical applications (e.g. batteries and fuel cells).

In this study we have examined the interfacial behaviour of several imidazolium- and pyrrolidinium-based ionic liquids. The surface tension at room temperature was measured with the pendant drop and Wilhelmy plate techniques. The interfacial tension of these ILs against a series of alkanes was determined by the pendant drop method. The contact angles on smooth Teflon surfaces were measured with the sessile drop method. Commercial grade ionic liquids (Merck) were used without further purification and these may contain significant amounts of impurities (mainly halides and water). Nevertheless the results are very reproducible and amenable to a simple physical interpretation.

The surface tension of all ILs studied strongly correlates with their molecular volume. The dependence is adequately described by the scaled particle theory. The interfacial tension measurements against apolar liquids allow the splitting of the surface tension into an apolar (Lifshitz–van der Waals, LW) component and an acid-base (AB) component. The Hamaker constants estimated from the LW components are in good correlation with the values calculated through the Tabor-Winterton approximation. With these results in hand, the contact angles measured can be fully predicted.

TIME-RESOLVED DIGITAL RADIOGRAPHY: CHARACTERISATION OF FLUID FLOW IN PAPER

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Containers for milk and juice (and similar products) are often manufactured from laminated polymer and board. The surface facing the liquid is typically coated with a plastic film to impart the necessary barrier properties to the container. However, during the process of folding the board into a container an untreated board edge is often left facing the liquid. This means that liquid may penetrate through the exposed edge and into the board.

Based on the need to quantify and compare all liquid-paper effects a technique has been developed to study imbibition using time-resolved digital radiography (TRDR). In essence, the method is based on monitoring the liquid uptake by taking a sequence of X-ray radiographs of a paper or board sample in contact with a liquid reservoir. This allows for an accurate determination of the liquid penetration rate and distribution as a function of time. Further, the use of X-ray imaging opens up opportunities to study the liquid imbibition in samples that previously has been difficult or impossible to study using conventional techniques such as imaging with optical light.

Results will be presented for a number of commercial and pilot board samples to illustrate the effect of surface treatment on the imbibition rate and distribution of fluid in these materials.

LIQUID TRANSPORT IN MULTI-LAYER FROTHS

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When bubbles of gas are sparged into an aqueous solution of surfactant in a column, a froth layer is formed above the layer of liquid. If water is injected into the rising column of froth at a particular position, two distinct layers are formed in the froth: a wet layer below the injection plane, and a dry layer above it. If water is injected at multiple points, any number of layers may be formed. In this study, a phase coexistence analysis was performed on the three-layer system. The liquid velocity was expressed as a function of the liquid volume fraction; this function included a term for entrainment without drainage, and a drainage term that quantified the interaction between the bubbles in the froth and the interstitial liquid. Predictions from this so-called drift-flux model were compared, using two different representative drainage terms, with one and two adjustable parameters respectively. The analysis was used to predict liquid fractions and superficial liquid velocities for the wet and dry froth zones. These were compared to experimental measurements performed with a laboratory froth column. Both versions of the analysis were in good agreement with experiment. That with the single-parameter drainage term (derived from the Richardson-Zaki equation) was marginally superior, and was also preferable for several other physical reasons. Theoretical predictions of the liquid fraction and overflow rate from the dry froth layer are supported by the data.

In addition, a similar drift-flux model was constructed for a rising coalescing froth, in which the bubbles increased in size as height in the froth increased, and the liquid fraction varied continuously with height. This model included the effect of the liquid released into the froth by coalescence. Profiles of liquid fraction and bubble size were obtained for a coalescing froth in a laboratory cell, and this data was found to support the predictions of the model.

NANOPARTICLE-PROTEIN INTERACTIONS: CONSEQUENCES FOR PROTEIN CONFORMATION, STABILITY AND AGGREGATION, AND FOR NANOTOXICITY

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Despite the remarkable speed of development of nanoscience, relatively little is known about the interaction of nanoscale objects with biological systems. Upon contact with a biological fluid, nanoparticles are immediately coated with a layer of proteins, and it is this adsorbed protein layer that a cell actually sees. Thus, it is the *amount and presentation* of the proteins on the surface of the nanoparticles that cause a biological response.¹

Detailed understanding of biological effects requires new approaches to the physical chemistry and theoretical interpretation of particle-protein systems. In particular, rates, affinities and stoichiometries of protein association with, and dissociation from, nanoparticles are important parameters for understanding the nature of the particle surface seen by the functional machinery of cells.

Detailed understanding of biological effects requires new approaches to the physical chemistry and theoretical interpretation of particle-protein systems. In particular, rates, affinities and stoichiometries of protein association with, and dissociation from, nanoparticles are important parameters for understanding the nature of the particle surface seen by the functional machinery of cells. Here we develop new approaches to study these parameters and apply them to plasma and simple model systems, albumin and fibrinogen. A series of copolymer nanoparticles with variation of size and composition (hydrophobicity) are used. We show that isothermal titration calorimetry is suitable for studying the affinity and stoichiometry of protein binding to nanoparticles. We determine the rates of protein association and dissociation using surface plasmon resonance technology with nanoparticles linked to gold via a thiol anchor, and through size exclusion chromatography (gel filtration) of protein-nanoparticle mixtures. This is less perturbing than centrifugation, and is developed into a systematic methodology to isolate nanoparticle-associated proteins.²

Depending on the type, strength and duration of the protein-particle complex, the protein conformation can be disrupted to different degrees, from almost no disruption, to slight spreading and domain swapping, to formation of a molten globule (loss of some tertiary structure), through to complete denaturation (loss of tertiary and secondary structure).³ This can have significant consequences for protein functioning and stability (aggregation).

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FORMATION AND DISRUPTION OF WORM-LIKE MICELLES IN MIXED SOLVENTS OF DIFFERENT POLARITY

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We have studied the structural and rheological behaviour of viscoelastic wormlike micellar solution in mixed nonionic surfactants, poly(oxyethylene) cholesteryl ether (ChEO₁₅)-triethylene glycol monododecyl ether (C₁₂EO₃) and anionic sodium dodecyl sulfate (SDS)-C₁₂EO₃ using a series of glycerol/water and formamide/water mixed solvents. The results are compared with that reported in pure water for the same system. The zero-shear viscosity first sharply increases with C₁₂EO₃ addition and then decreases, i.e. there is a viscosity maximum. The intensity (viscosity) and position (C₁₂EO₃ fraction) of this maximum shifts to lower values upon increasing the ratio of glycerol in glycerol/water mixed solvent; while the position of the maximum changes in a opposite way with increasing formamide. The oscillatory shear behaviour of the system can be described by the Maxwellian model in the region of low shear frequency and combined Maxwell-Rouse model at high shear frequency. The effect of temperature was also studied in ChEO₁₅/C₁₂EO₃ mixed surfactant system. Again, the zero-shear viscosity shows a maximum as a function of temperature, its position depending on the C₁₂EO₃ mixing fraction. Worm-micelles seem to exist at low temperatures (down to 0 °C) and high glycerol concentrations (up to 50 wt%), which is interesting from the point of view of applications such as drag reduction fluids. The results are interpreted in terms of changes in the surface curvature of aggregates and lyophobicity.

HEAT INDUCED AGGREGATION OF AMPHIPHILIC BLOCK COPOLYMERS IN AQUEOUS SOLUTIONS

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Amphiphilic block copolymers (ABCs) form micelles in aqueous solutions in analogy to conventional surfactants [1-2]. These micelles are thermodynamically and kinetically stable nanosized aggregates with core-shell morphology and can have different shapes like spherical, prolate/oblate ellipsoids, long rods etc. dependant on molecular characteristics and solution conditions. The present talk will provide an overview on the formation, characterization of nanoaggregates from ABCs and their applications.

Micellization and micellar characteristics of ethylene oxide-propylene oxide (EO-PO) based symmetrical triblock copolymers (PEO-PPO-PEO) is strongly temperature dependant. These features coupled with their interfacial characteristics and reversible thermorheological behaviour have led to their applications as carrier in drug delivery systems, template for metal nanoparticle synthesis and in preparation of mesoporous materials. Some results from authors' published work will be presented.

Polystyrene-polyethylene oxide diblock copolymer (PS-PEO) and Poly-2-(acrylamido)-2-methylpropanesulfonate-block-Poly-*N*-isopropylacrylamide block copolymers (PAMPS-PNIPAM) also form thermosensitive nanoaggregates in aqueous solution. Some recent unpublished results on the aggregation pattern of these diblock copolymers in aqueous solutions will also be presented.

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FORCED WETTING AND DEWETTING OF LIQUIDS ON SOLID SURFACES AND THEIR ROLES IN OFFSET PRINTING

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Forced wetting of a solid by a liquid is one of the most commonly encountered situations in many engineering applications. In this work, aspects and effects of forced wetting and forced dewetting are studied. Concepts of forced wetting and forced dewetting are used to explain the ink transfer principle in offset lithographic printing. In many previous studies, interfacial work of adhesion and work cohesion, as well as interfacial tension, have been used as criteria to predict ink transfer or non-transfer in offset printing. These criteria take no account of the dynamic nature of the printing process and could not explain some of the basic observations of ink transfer or non-transfer in offset printing. An alternative approach is taken in this study to take into account the dynamic nature of ink transfer and consider forced wetting and forced dewetting in an offset printing process. Adhesion strength is calculated and used as a criterion to predict whether ink will transfer or not. This work provides a comprehensive explanation of why ink can be transferred onto Teflon, a material that has lower surface free energy than ink.

Keywords: Forced wetting, forced dewetting, surface free energy, adhesion, offset printing.

BRIDGING THE MATERIALS AND LIFE SCIENCE DIVIDE: BIOINSPIRED COLLOIDAL SYSTEMS

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This presentation will focus on the construction of engineered colloids through the nanoscale modification of colloidal particles. These colloids, prepared by the sequential adsorption of charged materials, also known as the “Layer-by-Layer” technique, represent versatile systems for drug delivery and artificial cell research. It will be shown that a range of polymers can be employed to prepare these nanostructured materials, including synthetic (e.g., homopolymers, block copolymers) and natural (DNA) polyelectrolytes. This allows unprecedented control over the structure, composition and stability of the particles. It will be also demonstrated that polymers can permeate into nanopores of porous particles, and that following multiple polymer assembly steps and removal of the porous template, a new generation of interconnected nanoporous polyelectrolyte spheres can be prepared. These nanoporous spheres can sequester proteins at exceptionally high concentrations, making them of interest in enzyme catalysis. These studies are aimed at the construction of nanoengineered, bioinspired delivery particulate systems.

DENDRITIC POLYMERS AS DRUG CARRIERS

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Dendritic polymers are synthetic, branched polymers that are connected to a central core via a series of synthetic generations. In most cases, each generation expands the mass of the growing polymer by about two fold. The earliest dendritic polymers, known as dendrimers, were composed of multiple, perfectly branched polymers that could be traced back to a central core. The advantage of dendrimers is that the numerous termini created in their synthesis provide a multivalent surface that can be used in multiple ionic interactions with other molecules. Positive charged polyamidoamine dendrimers form a complex with DNA and are widely used for *in vitro* gene transfer reagents. Anionic dendrimers are being tested as inhibitors of HIV infections. Drugs, targeting ligands and imaging agents can also be attached to the termini to provide a multivalent and targeted drug carrier. The advantage is a high drug loading density on a low polydispersity carrier with macromolecular dimensions. Dendrimers can be synthesized with a high enough molecular weight so they are not eliminated in the kidney but remain small enough to leave the blood circulation and enter tumors or sites of inflammation. One disadvantage of placing a hydrophobic drug on the termini of the classical dendrimer is that the drug-loaded dendrimers may aggregate or associate with cell membranes; Hence may be eliminated rapidly from circulation. To circumvent exposure of the drug on the dendrimer surface, dendrons can be grown or grafted onto a preexisting polymer to create a dendronized polymer. Dendronized polymers greatly expand the range of polymer architectures that can be created and enable the synthesis of very high molecule weight polymers using classical polymer synthetic reaction schemes. The architectures can be linear, branched, bow-tie, hyperbranched or toroidal. In collaboration with the Jean Frechet Group at the University of California in Berkeley, we have explored the influence of water-soluble, biodegradable, polyester dendritic polymer architectures on polymer distribution in animals after intravenous administration. We attached doxorubicin via a hydrazone linkage to one dendron and poly(ethylene oxide) to the other dendron to create a 'Bow-tie' architecture. The pharmacokinetics and distribution of the Bow-tie dendronized polymers were greatly influenced by the balance of the number and MW of the PEO chains and the dendron generation. Bow-tie polymers with similar molecular weights but different MW PEO/number of PEO ratios were eliminated from circulation at different rates. Bow-tie polymers showed excellent drug accumulation in tumors as quantified by percent dose per gram tissue and tumor to muscle drug ratios. The antitumor effect of doxorubicin attached to a molecular weight optimized Bow-tie polymer was equivalent to doxorubicin encapsulated in a sterically stabilized liposome in the C-26 colon adenocarcinoma tumor model. Thus dendronized polymers display promising attributes as anti-cancer drug carriers and provide a platform for future improvements by combining targeting ligands and drug combinations or drug and imaging agents on the same polymer. Supported by NIH EB002047.

PARTLY-PEGYLATED POLY-L-LYSINE DENDRIMERS AS BIODEGRADABLE DRUG CARRIERS

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Dendrimers are highly organised and typically symmetrical structures approaching colloidal dimensions which show potential as drug delivery vectors. Dendrimer-based delivery systems have been suggested to provide i) extended circulation times (and therefore exposure) of rapidly cleared drugs and also ii) the potential for improved site specific (targeted) delivery. Dendrimers based on poly-L-lysine (PLL) offer the additional advantage of biodegradation, potentially reducing long term accumulation in target tissues and systemic toxicity. After intravenous administration, ‘uncapped’, amine terminated PLL dendrimers are metabolised to free lysine which in turn is reincorporated into protein biosynthetic pathways. Complete PEGylation of surface amine groups blocks dendrimer metabolism and facilitates enhanced urinary elimination of small (< 20 kDa) dendrimers and enhanced plasma circulation times of large (> 30 kDa) dendrimers. The focus of the current study was to examine the effect of partial (50%) surface PEGylation on the pharmacokinetics of ³H-labelled Generation 4 (16 surface lysines) PLL dendrimers after intravenous administration to rats. The ability of partly PEGylated PLL dendrimers to improve the plasma circulation time of the anticancer agent methotrexate (MTX) was also investigated in dendrimers comprising 50% surface PEG and 50% methotrexate. In these initial studies MTX was conjugated to the dendrimer via a stable (amide) linker. Partial surface PEGylation blocked the rapid vascular binding of PLL dendrimers apparent with uncapped (Lys₁₆(NH₂)₃₂) dendrimers although plasma concentrations still declined more rapidly than the fully PEGylated (Lys₁₆(PEG₅₇₀)₃₂) dendrimers due to facile urinary elimination. Metabolism of the PLL core was slowed, but not entirely blocked by the presence of 50% surface PEG groups (Lys₁₆(NH₂)₁₆(PEG₅₇₀)₁₆). Capping the residual cationic charge on 50%-PEGylated PLL dendrimers with acetyl groups (Lys₁₆(CH₃)₁₆(PEG₅₇₀)₁₆) further slowed metabolism of the PLL core, presumably by more effectively masking surface lysines from proteolytic attack. Attachment of MTX to uncapped sites on a 50% modified PEG₅₇₀ dendrimer via a stable (non-cleavable) amide linker (Lys₁₆(MTX)₁₆(PEG₅₇₀)₁₆) had little influence on the pharmacokinetics or metabolism of the dendrimer, however increasing the MW of the attached PEG to 1100 Da further increased the circulation time of the MTX-conjugated dendrimer and essentially blocked metabolism of the core poly-lysine structure. Partial (50%) PEGylation of PLL based dendrimers with 570 Da PEG therefore slows metabolism by shielding the PLL core from proteases, however, the PEG content is not sufficient to completely block metabolism. Increasing the size of the attached PEG chains to 1100 Da, however, more effectively blocks core metabolism and improves the circulation time of the drug-dendrimer complex. The results suggest that PLL dendrimers conjugated with 50% drug and 50% high MW PEG (>1100 Da) will improve the plasma circulation times of the conjugated drug and also allow for the eventual breakdown of the PLL core once cleavage of drug from the surface occurs.

INTERACTION OF DENDRIMERS WITH PHOSPHOLIPID BILAYERS

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Dendrimers are multi-functional synthetic biopolymers with numerous potential pharmaceutical applications, e.g. as drug carriers, anti-viral and anti-bacterial agents. However, the interfacial behaviour of dendrimers and mechanisms of dendrimer interactions with bio-molecules, cell membranes and solid particles are not well understood. The interaction of dendrimers with phospholipid membranes is of particular interest in understanding their behaviour *in vivo*. Biological membranes consist of a variety of positive, negative and neutral phospholipids, therefore the influence of membrane lipid composition may be significant in their interaction with dendrimers. Here we report a range of colloid and interfacial investigations on dendrimers aimed to gain insight into their biological activity and their effective formulation as pharmaceuticals.

Specifically, the adsorption of dendrimers on model phospholipid bilayers (liposomes) has been investigated, as well as the variation in liposome size and zeta potential. In particular, the influence of lipid composition, dendrimer generation and structure is explored. Phospholipid bilayer composition has been found to be important in the extent of dendrimer adsorption, particularly the inclusion of negatively charged lipids in neutral phospholipid bilayers. Similarly, both dendrimer size and architecture impacted on their interaction with lipid bilayers.

NOVEL ENGINEERING OF COLLOID PARTICLES FOR PHARMACEUTICAL SYSTEMS

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The common strategy for the production of colloid drug particles for a pharmaceutical dosage form is based on a growth of scale. The active molecule is engineered to a crystal form, the crystal form is then processed into particles, and finally the active pharmaceutical ingredients (APIs) are ‘formulated’ into the dosage form. The processing of colloidal particles typically requires the use of a destructive, energetic “top-down” technique to reduce the API to the required particle size range for a particular dosage form. Hitherto, only limited technological advances have been achieved for these processing techniques since their introduction in the post-war years in the late 1930’s. The approach to colloidal engineering involves extravagant use of resources and energy and more critically affects a whole range of physicochemical properties which ultimately govern the behaviour and stability of the colloids within suspensions and solid dosage forms.

While there is a high degree of reluctance within the industry to embrace and introduce new particle engineering technologies, there remains an ever increasing need to develop processes which specifically address the requirements for controlling the surface and bulk properties of colloid drug particles. This remains one of the key limitations for the future development of colloids and in particular nanoparticles for therapeutic applications within the pharmaceutical industry. The presentation will describe the current status of understanding of the underlying mechanisms which control the interfacial behaviour colloid particles and investigate the concepts and requirements for the successful development of new particle technologies in controlling and engineering organic colloids.

VALIDATING AFM ADHESION MEASUREMENTS IN A PHARMACEUTICAL APPLICATION

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Free-flowing powders are necessary in many pharmaceutical applications. For example, in the production of tablets, the ultimate dosage form, the ability of the drug-excipient powder mixture to flow easily into high-speed tablet presses is essential. Similarly, in dry powder inhalers a free-flowing powder will disperse more effectively leading to a more efficient, and uniform, delivery of the medication. Current dry powder inhalers deliver only approximately 20% of their drug payload to patients.

To formulate better performing powder mixtures requires an understanding of the relevant particle interactions, including capillary, electrostatic, van der Waals forces and surface energy effects. Atomic force microscopy (AFM) seems to be a suitable way in which to investigate these interparticle forces in the pharmaceutical area where the particles are on the micron scale. In 2000, Ibrahim et al. used AFM to study the adhesion forces between pharmaceutical particles and gelatin capsules,⁶ while in 2001 Louey et al. investigated the adhesion between lactose particles (the major excipient in both tablets and dry powder inhalers) and silica colloid probes.⁷ More recently, Hooton et al. applied JKR theory to AFM adhesion measurements between drug particles and highly oriented pyrolytic graphite and found a correlation between the work of adhesion between the different samples and the surface energies of the drug particles.⁸ However, this technique has not yet been validated for use with pharmaceutical particles by correctly applying the appropriate contact mechanics theory allowing direct comparison with independent measurements.

In this study, colloid probe AFM was used to measure the adhesive forces between lactose particles in a dry environment. A tip characterisation grating was used to reverse image the colloid probes. The surface energy derived from the application of JKR theory was found to be 42 mJ/m². This compares favourably with literature values of 39 – 41 mJ/m² obtained from inverse gas chromatograph measurements.

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TARGETING AND UPTAKE OF MULTILAYERED PARTICLES TO CANCER CELLS

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An area of research attracting a great deal of attention is the biofunctionalization of nano- and microparticles with specific cell targeting ligands for applications in sensing/diagnostics and in gene or drug delivery. In drug delivery, targeted particles have the potential to greatly improve the therapeutic qualities of existing drugs by delivering high doses of the therapeutic agent to the specific sites or cells where it is required, thus reducing undesirable toxic effects on other tissues or cells.

In this study, we developed fluorescent polymeric particles biofunctionalized with a specific antibody, huA33 mAb. The particles are prepared using the layer-by-layer (LbL) approach where a polymer film is assembled on a core 'template' particle which can either contain a therapeutic agent, or where the core can be dissolved and the therapeutic agent infiltrated into the resulting capsule. The targeting antibody, huA33 mAb, binds to the A33 antigen present on almost all colorectal cancer cells. 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 biofunctionalized, fluorescently-labelled particles/capsules to various human colorectal cancer cell lines.

It was found that the huA33 mAb-coated particles bound selectively to cells expressing the A33 antigen as demonstrated by a competitive binding assay. Upon binding, selective and time-dependent internalization of the particles was observed.

PHASE BEHAVIOR AND PHYSICOCHEMICAL INVESTIGATION OF SUCROSE ESTER MICROEMULSIONS WITH BOTANICAL ESSENTIAL OILS FOR POTENTIAL TOPICAL DELIVERY

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Sucrose ester microemulsions are one of potential candidates of cosmetic and drug delivery systems because of excellent biocompatibility and biodegradability, temperature-insensitive formation, thermodynamic stability, and improved solubilization of cosmetic and pharmaceutical actives. This study explores the phase behaviour and structural aspect of sucrose ester microemulsions containing botanical essential oils and determines the effect of the oil types and concentrations on the amount of solubilized water. Nonionic sucrose ester microemulsions composed of sucrose myristate (SM), isopropyl alcohol (IPA), and water were prepared with different types of essential oil such as eucalyptus oil and lavender oil. The pseudoternary phase diagrams were constructed by water titration at room temperature to obtain an optimal concentration of components for the microemulsion formation at different surfactant and cosurfactant mixing ratios ($K_m = \text{surfactant/cosurfactant}$) between 1:2, 1:1, 1.5:1, and 2:1. The microemulsion zone was found to be dependent upon the K_m ratios and types of essential oils. The single phase microemulsion zone increased when K_m ratio is increasing from 1:2 to 2:1 and no liquid crystal region was detected for both systems. The maximum water solubilization in microemulsion domain for eucalyptus and lavender oil was 80 and 67 wt. % of water at $K_m = 2.0$, respectively. Physicochemical properties of microemulsions containing a fixed oil/(SM+IPA) ratio of 0.25 were investigated by various experimental techniques such as dynamic light scattering (DLS), electrical conductivity, differential scanning calorimetry (DSC), pulsed gradient spin echo (PGSE) NMR and cryo-field emission scanning electron microscopy (cryo-FESEM). The results from all experiments showed the structural changes as the water content increases and indicated evidence of o/w microemulsion at 50 wt% of water for both oil systems. Microstructure studies suggested that transition from w/o to bicontinuous phase occurred in the range of 10 to 15 wt% of water and that the transition of bicontinuous to o/w phase occurred at ~ 45 wt% of water. The physical stability was also examined by centrifuge test at $10000 \times g$ for 30 minutes and freeze-thaw test at different storage temperatures (-5 to 70 °C) for 24 hours. All tested microemulsions were temperature-insensitive up to 70 °C and stable more than 6 months at room temperature without any phase change and separation. The structure and stability of sucrose myristate based microemulsions containing eucalyptus or lavender oil should be very interesting as new topical delivery systems.

COLLOIDAL DELIVERY SYSTEMS FOR SUBUNIT VACCINE DELIVERY - A PHARMACEUTICAL APPROACH PART 1: PHYSICO-CHEMICAL CHARACTERISATION

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With current gene and protein technology it is now possible to identify specific regions of some whole organisms which are likely to be recognized by the immune system, and to reproduce them synthetically as subunit vaccines. These so called epitopes are very safe because they are non-living but they also tend to be not very immune stimulating. To improve the immunogenicity of a poorly immunogenic antigen, our approach is to use colloidal delivery systems. Colloidal delivery systems are thought to enhance the immune response by more closely mimicking a virus or microorganism due to the possibility of multimeric antigen presentation and their large size compared to a subunit antigen.

In this presentation we will give an overview about the various colloidal delivery systems our group has developed for the delivery of subunit vaccines. We will describe new results in this field.

Our group has developed and characterised the following colloidal delivery systems:

- functionalised liposomes (mannosylated or including adjuvants such as Quil A),
- immune stimulating complexes (ISCOMs),
- cationic ISCOMs (termed Pluscoms),
- ISCOM implants,
- polymeric nanoparticles on the basis of microemulsions,
- in situ gelling chitosan solutions containing chitosan nanoparticles,
- cubosomes.

In the first part of this presentation we will describe and characterise these nanoparticles physico-chemically.

COLLOIDAL DELIVERY SYSTEMS FOR SUBUNIT VACCINE DELIVERY - A PHARMACEUTICAL APPROACH PART 2: IMMUNOLOGICAL TESTING

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Sub-unit vaccines consisting of peptide, protein or DNA are the future of immunisation worldwide. The advantages of sub-unit vaccines over traditional whole cell vaccines are improved purity and increased safety. However a major disadvantage of these vaccines, particularly with the peptide and protein vaccines, is their low immunogenicity and subsequent poor efficacy. A challenge for pharmaceutical science is to design formulations and delivery systems that can deliver the sub-unit vaccines to the immune system in such a way as to stimulate a protective immune response. One way of doing this is to incorporate the vaccine antigen into an immunogenic colloidal vaccine formulation.

Our group has developed and characterised the following colloidal delivery systems:

- functionalised liposomes (mannosylated or including adjuvants such as Quil A),
- immune stimulating complexes (ISCOMs),
- cationic ISCOMs (termed Pluscoms),
- ISCOM implants,
- polymeric nanoparticles on the basis of microemulsions,
- in situ gelling chitosan solutions containing chitosan nanoparticles,
- cubosomes.

Vaccine antigens were incorporated into a variety of colloidal delivery systems, including surface modified liposomes and immune stimulating complexes (ISCOMs).

In the second part of this presentation we will describe the immunological testing of these colloidal vaccine carriers.

CONTROLLED RELEASE TO THE LUNG: THE HOLY GRAIL OR WHOLLY IMPOSSIBLE?

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Many respiratory diseases follow circadian rhythms, where current treatments only allow rapid delivery over short time scales. For disease states, such as asthma in children, which manifest symptoms during sleep, the possibility of rapid drug delivery with extended release profiles offers a clear advantage over conventional medicaments. Furthermore, with advances in gene therapy, systemic delivery and the treatment of pathogenic respiratory infection, local controlled release would be a useful alternative to conventional dosage forms. This presentation highlights current issues and research related to controlled release inhalation therapy. Simple formulations were prepared and assessed in terms of aerosolisation efficiency and in vitro release rates. A series of polymer concentrations were investigated using different model drugs and in vitro models (e.g. USP paddle, flow through cell and diffusion models). Significant differences in the aerosolisation performance and release profiles of the model formulations were found. These variations could be related to the formulation components and apparatus used. In summary, evaluation of controlled release formulations needs serious consideration, in terms of materials used and testing methodology. These will be discussed.

ENCODED PEPTIDE ASSAYS: MERCAPTO-FUNCTIONALISED ORGANOSILICA MICROSPHERES AS A PLATFORM FOR PROTEOMIC ASSAYS

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Microsphere based biological assays have shown increasing potential as a decisive means of detecting and analysing biological interactions between genetic and/or proteomic elements. Such biomolecular interactions drive specific intracellular functions and often utilise surprisingly small structures as recognition motifs. As such, the growth, modification and rapid screening of motif analogues have become the stepping stone to understanding such critical biological systems and ultimately lead to the production of better diagnostics and pharmaceuticals.

Microsphere assays have provided researchers with useful tools for analysis of biological interactions owing to their ease of handling, reduced washing steps and the smaller sample volumes required for analysis. If optically encoded, such microspheres can be readily applied in multiplexed, flow cytometric assays for rapid detection and quantitation of specific interactions in complex solutions. While current assays can involve up to 100 optically unique microsphere sets, these supports cannot be applied toward organic synthesis. This is owing to their non-covalent incorporation and subsequent loss of optically encoding dyes from the polymer microspheres as they swell in organic solvents.

Organosilica microspheres with covalently coupled fluorescent dyes were characterised and trialed as peptide growth supports for the application toward immunoassays. The chemical stability, monodispersity and the structural consequences of silica condensation were investigated using SEM, XPS, Si29 NMR, BET and optical microscopy. The number of surface amine groups available for peptide growth was calculated by two independent analysis techniques. Five distinct microsphere populations were created by covalently coupling increasing concentrations of a fluorescent rhodamine dye derivative. Five peptides representing a small positional scanning library for the monoclonal antibody anti-myelin basic protein were directly synthesised on the encoded microspheres. A direct immunoassay was carried out and the specific and selective recognition of the correct epitope sequence was observed using flow cytometry. Such screening libraries have the potential as diagnostic devices, aiding the development of improved performance pharmaceuticals and the fundamentals of biological interactions.

POSTERS

POSTER SESSION SPONSORED BY ATA SCIENTIFIC

Poster SS-1

MIXED MONOLAYERS OF NTA DISULFIDE AND TEG THIOL ON GOLD NANOPARTICLE SURFACES STUDIED WITH OPTICAL SPECTROSCOPY AND ZETA POTENTIAL

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The stable functionalisation of colloidal gold nanoparticles with specific tethering surface units, e.g. nitrilotriacetic acid (NTA), has been employed to specifically attach nanoparticles to biologically relevant samples.^{1,2}

In the present study, we discuss the formation of mixed monolayers of NTA disulfide and triethylene-glycol (TEG) thiol on 16 nm citrate-stabilized gold nanoparticle surfaces in aqueous solution. Mixed monolayers of NTA/TEG provide a surface which both specifically tethers histidine tagged proteins and minimises non-specific binding of other proteins.³ The ratio of NTA to TEG on the nanoparticle surface can be examined by probing the surface charge using zeta potential measurements.

The use of 16 nm gold nanoparticles, which are larger than those used for previous NTA capping studies, provides strong plasmon absorption colour changes during nanoparticle aggregation. We studied the reversibility of the solution colour change to examine the steric and electrostatic stability of our modified colloids at various pH ranges. Additionally, 6,8-thioctic acid capped nanoparticles were examined as they provide a simpler system to study stability and pH effects.

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Poster SS-2

REAL-TIME RECORDING OF ANTIGEN-ANTIBODY REACTIONS AT SURFACES FOR IMMUNOASSAY MICROARRAY

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Protein arrays are rapidly becoming established as a powerful means to detect proteins, monitor their expression levels, and investigate protein interactions and functions. They are seeing an explosive progress and interest at the moment and have become one of the most active areas emerging in biotechnology today.

The development of new immunosensors based on antigen-antibody immunological reactions requires a stable and reproducible immobilisation of antigens on solid surfaces and characterisation of the affinity to antibody. With an imaging ellipsometer unlabelled antigen-antibody interactions were examined in-situ in a time resolved manner. Anti-Rabbit Ig, anti-Goat Ig, anti-Human Ig were immobilised on chemically modified silicon surfaces via biotin/streptavidin linkage. Optimisation of the blocking step for antigen binding allowed obtaining the highest signal: noise ratio in the assay.

Specific binding between antigens and its partners has been observed. The anti-Goat IgG interacts with Goat IgG like anti-Human IgG bound to human antibody. No immunological reactions were evaluated between human antibody and goat antigen.

Adsorption of Goat IgG on the goat antigen can be remarkably depicted by Langmuir's equation.

The ellipsometry results outline the possibilities of obtaining a controlled covalent binding of biomolecules to solid surfaces with an optimal stability and biological activity of the immobilized molecules with subsequent monitoring immunological reactions.

SPONGE AND LAMELLAR PHASES CONTAINING MIXTURES OF HYDROCARBON AND FLUOROCARBON SURFACTANTS

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Mixtures of hydrocarbon and fluorocarbon surfactants can show limited miscibility, forming for example coexisting populations of hydrocarbon-rich and fluorocarbon-rich micelles under some circumstances [1]. It is our aim to investigate this possibility of partial demixing in sponge and lamellar phases and the potential formation of novel structures.

Our system is based on the well-characterized lamellar and sponge phases of cetylpyridinium chloride, hexanol and 0.2 M brine [2], into which the partially fluorinated surfactant N-1H,1H,2H,2H-heptadecafluorodecylpyridinium chloride is incorporated. We investigated its effect on the surfactant membrane by probing the structures with small angle x-ray and neutron scattering (SAXS and SANS), while dynamic properties were characterized using dynamic light scattering.

We found that the hydrocarbon and fluorocarbon surfactants mix homogeneously in the sponge and lamellar phases with fluorocarbon/hydrocarbon ratios of up to 60 mol %, and their phase structure could persist without any observable changes. Surprisingly, not even the dynamics in the sponge phase region were affected by the fluorocarbon content, despite the fact that fluorocarbon chains are known to be much stiffer than hydrocarbon chains. Conversely, a small variation in the mixing ratio of co-surfactant/surfactant across the narrow sponge phase region resulted in significant changes to membrane flexibility.

At fluorocarbon/hydrocarbon ratios greater than 60 mol %, the sponge phase becomes turbid and phase separates; macroscopically, the lamellar phase remains within the single-phase region with partial demixing indicated by small-angle scattering data.

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Poster SS-4

SMALL ANGLE NEUTRON SCATTERING FROM CONCENTRATED PROTEIN SOLUTIONS INSIDE CELLS

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The interior of the human red blood cell (RBC) is a very concentrated solution, ~30% volume fraction, of the oxygen transport protein hemoglobin. While it is almost trivial to collect small angle neutron scattering from cellular suspensions, such systems are often so heterogenous to make such modelling meaningless as a probe of the intra-cellular solution structure¹. By considering the volume fraction and scattering length density of each cellular component in a suspension of whole RBC's in an isotonic media of 154mM NaCl it may be shown that scattered intensity is dominated by the intracellular solution of hemoglobin. This result agrees with conclusions drawn from the length scales associated with the anisotropy of the SANS pattern collected from a shear oriented suspension of red blood cells². The data is modelled by using a screened Coulombic potential to compute the solution structure factor³. The fitted intracellular ionic strength and hemoglobin charge are compared with those measured by other methods.

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CHARACTERISATION OF ALKYL-FUNCTIONALISED Si(111) USING REFLECTOMETRY AND AC IMPEDANCE SPECTROSCOPY

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The past few years have seen a dramatic increase in the number of organic thin-film systems being studied that are based on Si-C covalent bonds, for biopassivation or biosensing applications. This approach to functionalising Si wafers is in contrast to Si-gold-thiol or siloxane chemistries and has been shown to lead to densely packed alkyl monolayers.¹⁻³ We have produced a series of alkyl monolayers (from decane to octadecane) that are directly covalently bonded to the surface of Si(111) wafers. The structure of these surfaces were studied using X-ray reflectometry and AC Impedance Spectroscopy. The combination of these techniques are able to probe the thickness, density and surface roughness with atomic resolution. Fundamental physical properties of these films such as chain canting angles and area per molecule can be determined. Results from these distinct yet complementary characterisation techniques are compared and discussed in relation the surface chemistry and as a function of alkyl chain length.

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POSITRON ANNIHILATION LIFETIME SPECTROSCOPY AND SMALL ANGLE X-RAY SCATTERING OF SELF-ASSEMBLED AMPHIPHILES

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Amphiphile self-assembly materials can possess complex internal nano-structure. The exact nature of the internal structure is governed by the geometric packing constraints of the self-assembling amphiphilic molecules, controlled by nano-scale physical and chemical interactions, and when an equilibrium packing arrangement is achieved the resulting thermodynamically stable phase is often one of relatively well defined geometry. There is a wide spectrum of phase structures that are potentially formed by a given system of this type. These assemblies span micelles, cubic and hexagonal phases, L₃ sponge phases and bicontinuous microemulsions; all with quite different properties as a result of their nano-structure. In the case of lyotropic liquid crystalline materials, in particular, the internal nano-structure imparts a very high surface area to the material, which consequently lends itself to applications where nano-dimensions and a well defined interface are key performance criteria. An example of one such material is based on phytantriol and water.

We have conducted positron annihilation lifetime spectroscopy (PALS) and small angle X-ray scattering experiments on a phytantriol-water (89/11 w/w %) system as the system undergoes a lamellar to isotropic liquid (reverse micelles) phase transition *ca.* 35°C. The pore size and size distribution measured by PALS will be compared with SAXS data and discussed in terms of the LC phase transition and the accompanying internal nano-structure changes within these phases. These internal nanostructure changes are of keen importance to us as we focus on the use of ordered amphiphile self-assembly materials in many applications, including drug delivery and structure-templates for the creation of mesoporous separation, catalysis and energy storage materials.

MANIPULATION OF SURFACE ADSORPTION USING POLYELECTROLYTE / SURFACTANT MIXTURES

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The strong surface interaction between polyelectrolytes and surfactants of opposite charge give rise to a complex pattern of adsorption and surface tension behaviour. Neutron reflectivity and surface tension have been used to investigate this behaviour at the air-solution interface, and a number of different systems have been investigated.

Complementary studies on the cationic polymer, polyDMDAAC, and anionic surfactant, SDS, and the anionic polymer poly(styrene sulfonate), PSS, and the cationic surfactants, C_nTAB, show dramatically different behaviours which are characterized by surface depletion and surface layering of polymer / surfactant complexes respectively. It is shown how this range of surface behaviour can be rationalized in terms of the competition between the formation of surface-active polymer / surfactant complexes and solution polymer / surfactant micelle complexes.

For a range of pH sensitive polyelectrolyte / surfactant mixtures (poly(ethyleneimine), PEI / SDS, poly-L-lysine, PLL, / SDS and poly(acrylic acid), PAA, / C_nTAB) the relative importance of the polymer architecture / conformation and the electrostatic and hydrophobic interactions between the polymer and surfactant will be highlighted.

A relatively simple theoretical treatment, based on the law of mass action, will be described. It will be shown how most of the pertinent features of the complex range of surface tension behaviours encountered can be explained by this mode

IN SITU INFRARED SPECTROSCOPIC ANALYSIS OF ADHESION PROCESSES OF SMALL MARINE ORGANISMS

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Many marine organisms use adhesive polymers to form strong surface attachments under water. The adhesion process is greatly complicated by the difficulty in displacing water from the adhesive interface and the problem in dealing with water's ability to weaken many forms of chemical bonds. Despite that, the remarkable feature of these adhesive polymers includes the ability to achieve long-lasting adhesion in a wet environment and adherence to virtually all types of inorganic and organic surfaces. Mussels, barnacles and tubeworms secrete cement protein when they settle on the surface of a rocky substrate and materials such as ship hulls. Furthermore, the cosmopolitan intertidal green alga *Ulva* needs to bind to a surface quickly in order to complete its life history.

These organisms often attach themselves to man-made structures causing corrosion and fouling on many marine infrastructures. Hence, the need to comprehend the role of specific functional groups involved in the adhesion process. Our previous studies have been carried out with common blue and New Zealand Greenshell™ mussels, placed in a flow cell containing a ZnSe prism and supplied with temperature-controlled seawater. Their adhesion has been investigated by *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy. Different absorption spectra were obtained when the mussels were predominantly moving across the surface or forming permanent bonds. However, it was observed that the absorption of infrared radiation by the aqueous solutions flowing over the crystal resulted in temperature increases close to the prism surface. This increase was of concern as it has the potential to alter the behavior of the marine organisms, which had been kept at 12°C (the temperature of the ocean hereabouts).

In order to address this concern a new flow cell has been developed which has coolant flowing within channels of the stainless steel crystal mounting of the ATR accessory. The ATR flow cell was horizontal and designed to enclose a multiple internal reflection germanium crystal. Thermocouples were used to measure the temperature inside the cell, as well as that of the cooling water and of the solution containing the marine organism. We present results for studies of the adhesion of *Ulva*, barnacles (*Balanus galeatus*.) and tubeworms (*Phoronids*). Infrared absorption bands for proteins and polysaccharides were chosen as these macromolecules are major constituents of biofilms. Spectra at different temperatures and with different prism materials (germanium rather than ZnSe) were recorded. The ATR-IR technique permits examination of the early stages of adhesion of marine organisms. This is a novel approach and has wide potential for gaining new knowledge about bioadhesion processes.

SMALL-ANGLE X-RAY SCATTERING STUDIES ON STRUCTURE OF AN ENZYME PROTEIN IN SOLUTION

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To understand the conformational behavior of a protein, it is necessary to define not only the structure of its native state but also that of various denatured states. Recent studies have revealed the biological significance of denatured states in processes such as aggregation, chaperone binding, and transport across membrane. A variety of denatured states have also been identified, differing in their overall dimensions and the extent of residual secondary and tertiary structures. In particular, pepsin is a good model for the study of conformational behavior under various conditions because detailed information can be obtainable on the secondary structure, enzymatic properties, and zymogen activation. In the present study, we carried out solution X-ray scattering (SAXS) experiments on porcine pepsin, which is a gastric aspartic proteinase that plays an integral role in the digestive process of vertebrates, in order to obtain detailed information on the overall structure of porcine pepsin at the native state and its structural changes in solutions of various pH values. The solution SAXS data were analyzed in detail, providing important information on the structure and variations with pH conditions. From the SAXS profiles and determined parameters, structural models of the porcine pepsin were reconstructed, which was made inside the search volume of maximum diameter D_{max} calculated from the $p(r)$ function. The reconstructed models were obtained without imposing any restrictions on the symmetry and anisometry of pepsin molecule. Under several pH conditions, the reconstructed models reveal various conformational states, when compare to the crystal structure. The structural differences between solution and crystal structure of pepsin can be account for the inherent conformations of the flexible subdomain under carefully controlled specific pH conditions.

This study was supported by the Korea Science & Engineering Foundation (National Research Lab for Polymer Synthesis & Physics and Center for Integrated Molecular Systems) and by the Ministry of Education (BK21 Program). Synchrotron GIXS measurements at the Pohang Accelerator Laboratory were supported by the Ministry of Science & Technology and the POSCO.

Poster SS-10

INFLUENCE OF A POLYMER DEPRESSANT ON THE WETTABILITY OF MODEL SURFACES

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The effect of a polyacrylamide-based depressant on the wettability of model surfaces with different hydrophobicity was investigated using the captive bubble method. The quality of the surfaces (single and two-component SAMs with methyl and hydroxyl end- groups) was confirmed by FTIR, contact angle and AFM prior to the polymer adsorption. External reflection FTIR was used to determine the surface concentration of hydroxyl and methyl groups by comparing the ratio of areas of $-\text{CH}_3$ (methyl group) and $-\text{CH}_2$ (methylene group) asymmetric peaks. In situ tapping mode AFM was used to image the adsorption of the polymer in-situ and to collect data about the morphology of the polymer and the thickness of the adsorbed layer. Correlations are drawn between the morphology of the adsorbed layer and the ability of the polymer to reduce the contact angle. External reflection FTIR was also used to investigate the binding of the polymer to the thiol covered substrate.

NETWORKS OF LIQUID BRIDGES IN WET GRANULAR SYSTEMS

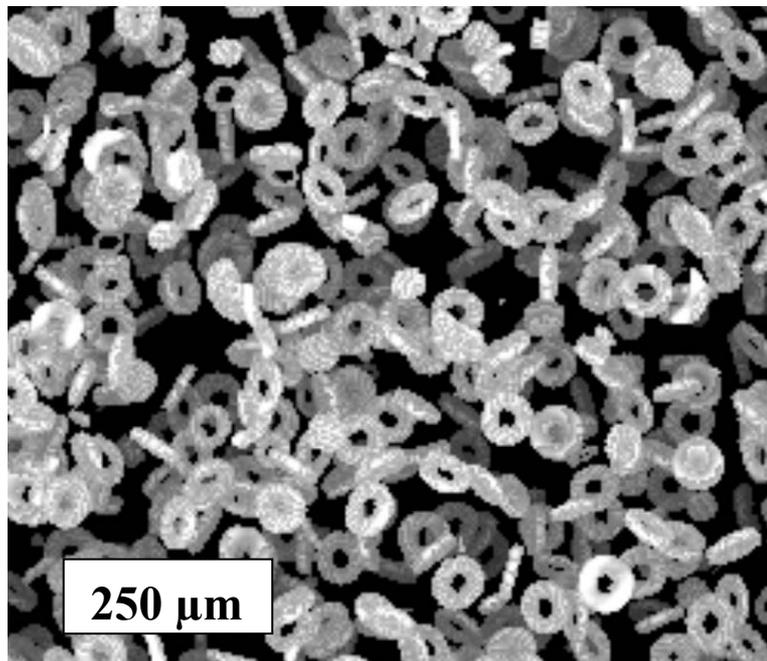
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The macroscopic mechanical properties of a dry granulate change dramatically when small amounts of liquid are added, as everybody knows from the construction of sand castles [Nature 387, 765 (1997)]. This is due to capillary bridges forming between mutually adjacent grains in the pile, which exert an attractive force by virtue of the surface tension of the liquid. Although the tensile strength of wet granulates can be roughly estimated from these forces, a quantitative theory of the mechanical properties of the granulate requires a detailed understanding of the topology of the complex network of capillary bridges. Furthermore, the relative importance of dissipation due to the rupture of bridges and due to viscosity of the liquid for the macroscopic viscosity and yield strength of the material is presently unclear.

We have applied x-ray microtomography (50 keV) to image the liquid structures forming in random piles of glass microspheres wetted by different fluids. Upon increasing the fluid content, transitions to clustering and percolation can be directly observed. The relation between the inner liquid surface and the yield stress is discussed.



X-ray tomography image showing liquid bridges (bright “doughnuts”) between granules consisting of monodisperse glass spheres (not visible).

INTERACTION AND STABILITY OF BINARY MIXTURES OF CATIONIC AND NONIONIC SURFACTANTS: INTERFACIAL TENSION AND FLUORESCENCE PROBE STUDIES

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Interaction and stability of cationic surfactants cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPyBr) with non-ionic surfactant decanoyl-*N*-methylglucamide (Mega-10) have been studied at different mole fraction of α_{CTAB} or α_{CPyBr} by using interfacial tension (γ) and fluorescence probe technique. From γ vs. $\log C_s$ plots, the values of critical micellar concentration (*cmc*) and various interfacial thermodynamic parameters has been evaluated. The experimental *cmc* was analysed with pseudophase separation model and the regular solution theory. Experimental *cmc* values deviate negatively from ideal *cmc** values in both binary mixtures indicating the presence of synergism in the mixed micelle formation. This synergism is slightly more favourable in CTAB+Mega-10 than those of CpyBr+Mega-10. The interaction parameters in the mixed micelle (β_{12}^{mic}), in the mixed monolayer (β_{12}^{σ}), the micelle composition (X_1^{mic}) and monolayer composition (X_1^{σ}) at different α_{cationic} were computed. According to Maeda's approach, the parameter B_1 related to the standard free energy change associated with the introduction of one ionic species into a nonionic micelle coupled with the release of one nonionic species from the micelle have been evaluated.

By using static quenching method, the mean micellar aggregation number of pure and mixed micelles of CTAB + Mega-10 was obtained. It has been observed that N_{agg} of mixed micelles deviates negatively from the ideal behaviour (Fig. 1). It is to be noted that N_{agg} of CPyBr is not determined because CPyBr itself act as a quencher. The micropolarity of the micelle was monitored with (I_1/I_3) ratio and found to be increase with the increase of ionic content indicating the polarity of the core of mixed micelle increases as the ionic content increases. The microviscosity of fluorescence probe Rhodamine B (RB) was monitored by fluorescence anisotropy (r) at different α_{cationic} . The results indicate that the participation of the ionic surfactant forms slightly more rigid structure than those of pure micelles, although the magnitude of r value for CPyBr+Mega-10 is slightly higher than those of CTAB+Mega-10.

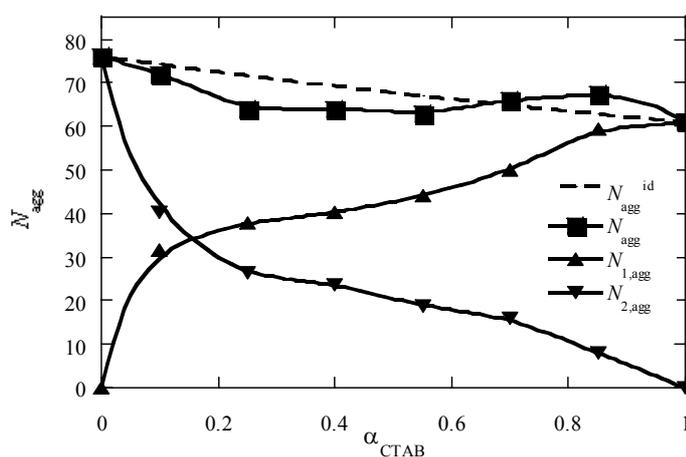


Fig. 1. Plot of N_{agg} vs. α_{CTAB}

Poster SS-13

**USING ATR-IR TO DETERMINE THE MECHANISM OF
ADSORPTION BY A PERFLUOROSULFONIC ACID ONTO A Pt
BLACK THIN FILM**

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Proton exchange membrane fuel cells (PEMFC) are the focus of much research. They appear to be the best prospect for a lightweight, portable fuel cell for use in the automotive industry. One of the main areas of interest is the performance of the electrode assembly, which comprises two platinum electrodes bonded to a central proton exchange membrane. The benchmark membrane material is Nafion® a perfluorinated sulfonic acid polymer whose behaviour is greatly influenced by interactions involving ionic domains formed by the sulfonic acid terminated side chains. Although Nafion is used commercially in fuel cells there are still many points of conjecture regarding its' chemistry and morphology. In this ATR-IR study we used a model compound (perfluoro(2-ethoxyethane)sulfonic acid) to mimic the ionic side chains of Nafion with a view to improving the understanding of the role that they play in the formation of the electrode assembly.

SOLVATION LAYERS IN ROOM TEMPERATURE IONIC LIQUIDS

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Solvation force profiles for three ionic liquids (ethylammonium nitrate, propylammonium nitrate, and 1-ethyl-3-methylimidazolium acetate) confined between Si_3N_4 tips and mica, silica and graphite surfaces have been measured using a standard atomic force microscope operating in deflection mode. The measurements reveal oscillatory behaviour in all cases (E.g. Figure 1), with the size of the oscillations corresponding to the physical dimension of the ionic liquid molecule. Comparison of results obtained on different surfaces allows the level of interaction between the ionic liquid and the substrate to be inferred.

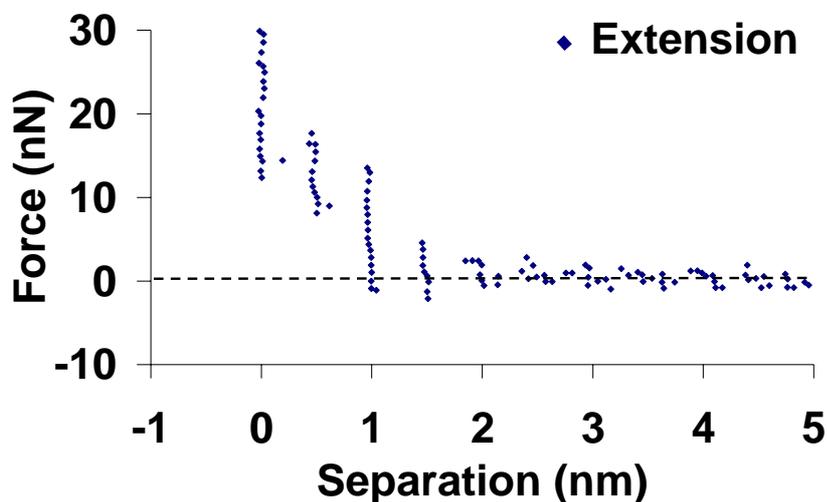


Figure 1. Force versus distance profile for an AFM tip approaching a mica surface in ethylammonium nitrate.

ATOMIC FORCE MICROSCOPY STUDY OF FLY ASH ADHESION: ADDRESSING INDUSTRY PROBLEMS

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Fly ash is the unburned portion of fuel produced by coal fired power stations and can cause significant environmental problems. Two significant fly ash related issues have come to light from local industries in Central Queensland. The first has to do with improving the efficiency of fly ash capture to prevent its release into the atmosphere. The other problem involves preventing fly ash from clinging to conveyor belts beyond the delivery point and hence falling off further along the belt. It is clear that in both of these processes the interaction forces dictating fly ash adhesion are important and need to be considered and understood to arrive at satisfactory solutions. In an effort to understand the nature of fly ash adhesion we have undertaken an experimental study utilising the atomic force microscope (AFM) to quantify the interaction forces between fly ash particles and the materials they come into contact with.

Most fly ash is in the form of alumino silicate spheres and therefore lends itself well to use as a colloid probe in the AFM. In addition we have used a number of other techniques, such as SEM, EDS and XRD to probe the bulk material properties. Although we are mainly interested in the surface interaction, this complementary bulk material information enables us to select suitable particles for attachment to the cantilever. One of the complicating factors in the treatment of the data is the observation that fly ash particles are often decorated with smaller particles, thus introducing geometry issues.

Both of the processes we are interested in are complex. For instance, when fly ash is removed from the hot flue gas by electrostatic precipitators the particles are artificially charged to ensure that they are attracted to the oppositely charged collection plate. However, when the particles reach the collection plate both electrostatic and van der Waals forces play a role in preventing the fly ash from re-entrainment in the gas stream. In the other case, the fly ash is carried on a conveyor belt where it is being sorted, compacted, and charged. We do not purport to be in position to model all of these processes. This poster concentrates on our attempts to characterise and understand the fundamental interactions that fly ash particles experience when they are collected and transported.

NEAR CONTACT INTERACTIONS BETWEEN COLLOIDAL PARTICLES USING LASER TWEEZERS

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The micromanipulation and force measuring capabilities of laser tweezers provide the ability to probe the mechanics and interactions of colloidal materials on nanometer to micrometer length scales. I will present recent work that uses laser tweezers to investigate the mechanical properties and microrheology of particulate gels. Our approach focuses on characterizing the micromechanics of aggregates that mimic the stress-bearing backbone in gels. These experiments provide an important bridge between the nanometer scale interparticle interactions and interfacial phenomena to the macroscopic rheological properties of gels. Furthermore, due to the small separations between particles in gels, the interactions are expected to deviate significantly from typical models of colloidal forces, such as DLVO.

Using time-shared optical traps, backbone mimics are directly assembled in salt solutions into precisely controlled geometries. The aggregate bending rigidity is then measured using a three-point geometry of traps. We find that aggregates behave elastically up to a critical bending moment, after which they exhibit small stick-slip rearrangements. The linear bending rigidity is found to be sensitive to the particle surface chemistry, ionic species and ionic strength. The bending rigidity between individual particles agrees with the JKR model of particle adhesion, providing a direct link between the micromechanics and the interfacial adhesion energy of the particles. This enables the use of reasonable models of the adhesion energy to predict the bulk elastic modulus of gels.

The non-linear bending mechanics of aggregates are also of significant interest, since they represent the microscopic processes that underlie the yield stress, creep recovery and delayed sedimentation of gels. We identify a critical bending moment at the point of the stiction-like rearrangement of a single colloidal bond. These mechanics are consistent with the local shearing force overcoming the static friction force between neighboring adhesive particles. We show that this newly identified nanoscale phenomenon provides a *quantitative* basis for understanding the macroscopic shear yield stresses of strongly flocculated polystyrene latex gels [1], based on the maximum bending moment exceeding the critical moment the constituent colloidal bonds of the gel microstructure. This results in a direct relationship between the rheology of these gels and the boundary friction between Brownian particles.

Overall, these experiments enable us to bridge macroscopic rheology of colloidal gels to the underlying microstructural response. Furthermore, the new insight we have gained provides useful strategies for tailoring gel properties through the rational manipulation of the nanometer scale near-contact interactions between Brownian particles.

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**ANISOTROPIC CHANGES IN PORE MORPHOLOGY AND FLUID FLOW
OF COMPRESSED ARTICULAR CARTILAGE STUDIED BY
FLUORESCENCE RECOVERY AFTER PHOTBLEACHING (FRAP):
IMPLICATIONS FOR JOINT LUBRICATION**

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Cartilage sections of thickness 30 μm cut from the middle zone of pig knee articular cartilage and infused with buffer solution containing fluorescently marked 70 kDa dextran were compressed between two sapphire surfaces in a 'pressure cell' under different loads (pressures). The resulting compression (strain) and change in pore volume were measured as a function of time simultaneously with measurements of the changing lateral diffusion of the dye molecules using Fluorescence Recovery After Photo-bleaching (FRAP). Our results show that the highly anisotropic structure of cartilage – which consists of large columnar (cylindrical or tubular) pores oriented normal (perpendicular) to the surface, each bounded by a porous network of trellis-like collagen fibrils – has a strong effect on the way fluid flows laterally and normally at different stages of compression. With increasing compression (load, strain) the pores of the trellis-like cylindrical walls close up, thereby changing the lateral (radial) flow occurring through these pores to normal (axial) flow out from the cartilage surface. The diffusion and flow of fluid in the cartilage porous matrix of the middle zone are almost unaffected by low compressions (strain <50%), but with increasing strain and pressure (>0.5 MPa or 5 atm) water is effectively 'pumped' normally out from the cartilage surface. This outward 'weeping' flow prevents the collapse of the fluid film between the cartilage and opposing surface, which helps considerably in the lubrication and wear resistance of the delicate superficial zone layer of the cartilage surface at high loads. Increased focus on the composition and other properties of the different fibril structures in cartilage may lead to a fuller understanding of the breakdown of joint lubrication systems, in parallel with ongoing studies on the functions of their constituent molecules (hyaluronic acid, lubricin, lipids, etc.).

Poster SF-5

HYDRODYNAMIC BOUNDARY CONDITION FOR HYDROPHILIC AND HYDROPHOBIC PARTICLES

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We describe measurement and interpretation of the hydrodynamic force acting on a sphere approaching to, and withdrawing from a flat plate in viscous concentrated aqueous sucrose solutions ($0.001 \text{ Pa s} < \eta < 0.080 \text{ Pa s}$). We study both hydrophilic and hydrophobic systems with specific interest in the hydrodynamic boundary condition. Compared to earlier studies of hydrodynamic forces on small particles, we reduce the uncertainty in the absolute particle – plate separation by using an evanescent-wave measurement of the separation

THE STRUCTURE OF SYNTHETIC TROPOELASTIN SURFACES

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Elastin is a key extracellular matrix protein found within skin, lungs, bladder, elastic cartilage and arteries. It is principally synthesised during the development or growth of tissues, with tropoelastin expression occurring during mid- to late fetal or embryonic periods. Elastin is remarkably stable in healthy tissue, with an estimated half-life of 70 years, making it the most persistent protein in the human body. Elastin plays an essential role in tissue biomechanics, providing a combination of strength and flexibility, as well as modulating a variety of cellular and protein interactions.

The importance of the major properties of elastin to the field of tissue engineering has been illustrated by recent biomaterial designs. Significantly, despite its notable characteristics elastin is currently critically lacking from tissue-engineered grafts. Major challenges to the use of native elastin result from its substantial insolubility. These are compounded by its highly crosslinked nature and contamination with tightly associated proteins.

We have recently demonstrated that synthetic elastin sheets can be produced from the same building blocks as native elastin; a protein called *tropoelastin*. Although a common material in the human body, very little is known about the structure of tropoelastin at the molecular level. To date, no crystal structure studies have been reported. Using a number of techniques we have assembled molecular films of tropoelastin on a variety of solid surfaces and studied their structures using AFM, X-ray and neutron reflectometry. By modifying surface characteristics of our substrate materials we have gained a deeper understanding of the structure of tropoelastin as well as gaining some insight into the mechanism of cross-linking to form synthetic elastin biopolymer.

ADSORPTIVE IMMOBILIZATION OF ACETYLCHOLINESTERASE: INHIBITION STUDIES

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Acetylcholinesterase (AChE) is an enzyme that is found in the synaptic cleft. This enzyme role is to terminate the nerve impulses transmission by hydrolyzing the acetylcholine (ACh) to choline and acetic acid and considered as an ultimate target for various kinds of medicines and even toxicants especially carbamates. Adsorptive immobilization of electric eel derived acetylcholinesterase was achieved by using hydrophobized silica-based matrices. Adsorption efficacy was evaluated through saturation studies in which synthesized alkyl substituted nano porous silica was found to saturate at 11.5 mg protein / g matrix by enzyme. Effect of less polar medium on adsorption process and operational properties of immobilization product in the mixture of water/ water miscible organic solvent has been included. Based on our comparative results thermal stability and inhibitor sensitivity of the immobilized acetylcholine esterase was improved effectively in comparison with the free form.

Keywords: Acetylcholinesterase, adsorption, inhibition, stability, immobilization

Poster SF-8
**DYNAMIC FRICTION FACTORS IN PARTIALLY WETTING
SYSTEMS**

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The importance of wetting and dewetting processes to a vast number of industrial applications has been well recognised, but the mechanisms involved and the control factors related are still not well understood and predictive models are limited.

In this work, dynamic contact angles of water and squalane advancing over two surfaces, polyethylene terephthalate (PET) and an amorphous fluoropolymer (Teflon AF1600), were determined over a velocity range of four orders of magnitude using the Wilhelmy Plate Technique. The contact angle – velocity data were described by the molecular kinetic theory of wetting (MKT). The advancing contact angles were calculated by extrapolation to zero velocity and corresponded to those measured by the sessile drop technique. Special care was given to the data fitting in order to reliably extract the principal parameters of the MKT (i.e. the average molecular displacement distance, λ , and the quasi-equilibrium displacement frequency K_0) by employing the ‘bootstrap’ fitting technique, which revealed a strong correlation between K_0 and λ . The dynamic friction factor $\zeta = k_B T / K_0 \lambda^3$ proved to be more suitable to describe the dynamic wetting process than the two individual parameters. ζ was found to depend on the static wetting properties of the system as well as the viscosity of the liquid.

FROM REPULSION TO ATTRACTION: SURFACTANT AGGREGATES WITH POLYMERIC VS. SIMPLE MONOVALENT COUNTERIONS

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Oppositely charged polymer-surfactant pairs are used extensively in formulations. Representative examples are formulations where one wishes to deposit water-insoluble surface layers on textiles, hair or skin. A fruitful approach to the problem of water solubility vs. insolubility of such complex surfactant mixtures is to ask: *How are the interactions between charged surfactant aggregates affected by polymeric counterions?* In our systematic experimental study of this problem, we employ a maximally simplified strategy where the pure “complex salt” (surfactant ion + polymeric counterion) is our point of departure [1-5].

Some of the insights that have emerged from these studies concern

- relations between surfactant phases and structures formed in the absence or presence of polymeric counterions
- the importance of the size and shape of the surfactant aggregate for the maximum water uptake of the formulation
- how the charge density of the polymeric counterion affects shapes and interactions of surfactant aggregates
- how surfactant aggregates with polymeric counterions can be used as model colloids for fundamental studies

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NANOPARTICLES AND NANOTUBES MODIFIED SCANNING PROBE MICROSCOPY TIPS

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Presented will be some recent developments in the scanning probe microscopy tips modification.

First, we have developed a wet-chemistry procedure to attach a 10~40 nm colloidal gold nanoparticle to the top of a scanning probe microscopy (SPM) probe tip, making experiments of single nanoparticle interaction possible.¹ This procedure of particle attachment is flexible and can be modified to attach nanoparticles of different kinds and sizes. The single nanoparticle terminated tips have also the potential for various other applications, such as, probes of enhanced sensitivity for optical and magnetic modes SPM.

Second, we have developed carbon nanotubes modified atomic force microscopy (AFM) tips which allowed for the controlled penetration through the living cells membranes. Nanotube modified tips were coated with a thin carbon layer for enhanced strength and a second layer of gold coating allowing easy chemical modification. Test experiment on cell cultures demonstrated that the tips could penetrate the cell membrane at indentation depth as low as 100 - 200 nm with minimum impact on the cell functions. The nanotube tips indenters could find applications for genes and molecular delivery, cell membranes characterization and in the bioelectrochemical research.

1. I.U. Vakarelski and K. Higashitani *Langmuir* **2006**, 22, 2931-2934.

Poster OX-1

**THE NUCLEATION, GROWTH AND PARTICLE INTERACTIONS OF
Al(OH)₃ DURING CRYSTALLIZATION FROM SYNTHETIC
SUPERSATURATED CAUSTIC ALUMINATE LIQUORS**

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Several, fundamental studies providing new knowledge and greater understanding of the mechanisms of nucleation, growth and agglomeration of aluminium tri-hydroxide (Al(OH)₃) crystals from synthetic, optically-clear, supersaturated caustic aluminate liquors have been performed to elucidate the inherently slow gibbsite (γ -Al(OH)₃) crystal growth kinetics. Isothermal properties, crystallization behaviour and species/particle interactions of self-nucleating, dilute and industrial strength (Bayer liquor type) solutions were characterized and quantified as a function of supersaturation, ionic strength, temperature and caustic type (NaOH vs KOH) solutions and time.

Models describing the mechanisms of Al(OH)₃ crystallization (nucleation, growth and agglomeration), based upon novel, poly-condensation crystallization and particle interactions theory, are proposed from several results gleaned from extensive investigations involving solution speciation, static and dynamic light scattering, x-ray radiation, rheology and colloid probe atomic force microscopy. The significance and implications of the findings for the Bayer process gibbsite crystallization process prevailing in alumina refining industry are highlighted and discussed.

Poster OX-2

SUPERPARAMAGNETIC OXIDE NANOPARTICLES FOR USE AS MRI CONTRAST AGENTS

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Magnetic Resonance Imaging (MRI) is currently the non-invasive imaging technique of choice for physicians investigating soft tissue injury. Superior spatial resolution and the capacity to differentiate soft tissue and organs have placed MRI at the forefront of clinical diagnosis. The contrast afforded by MRI relies upon the enhancement of local water proton relaxation times T_1 and T_2 . When there is poor contrast between healthy and diseased tissue, the use of a contrast agent is required. Contrast agents, the magnetic resonance equivalent of a dye, are molecules/particles injected into the body that alter the local water proton relaxation times and increase contrast between normal and pathological regions. Whilst some partitioning of contrast agents does occur, which allows diagnosis for certain organs, they are generally non-tissue specific. There is significant need therefore for better contrast and target specific contrast agents. In the current work we have synthesised a number of different superparamagnetic oxide materials as targeted MRI contrast agents in order to optimise MRI contrast. Structure property correlations have been made as a function of relativity, aspect ratio and size in order to optimise efficacy of the particles. Further work to provide target specificity is continuing.

Poster OX-3

THE SELECTIVE ADSORPTION AND ITS BIOLOGICAL IMPACT OF TITANIUM OXIDE SURFACE

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The surface of titanium implants is in direct contact with host tissue and plays a critical role in determining biocompatibility. One approach to promote cellular adhesion on titanium (Ti) is to modify surface of titanium with ECM proteins to enable specific cell-ECM interaction. Fibronectin (FN) and vitronectin (VN) are major cell adhesive proteins found in the extracellular matrix (ECM) of various tissues, and in circulating blood. This study evaluated the engineered biomimetic surface of titanium by using recombinant FN and VN that contains the binding site for integrins. MC3T3-E1 cells seeded upon the rFN-coated titanium showed a marked increase in cell adhesion, proliferation, and differentiation over rVN-coated titanium. Furthermore, we correlated the improved biocompatibility of rFN-coated titanium to the 3-fold preference of surface properties of titanium for rFN over rVN ($p < 0.05$) in protein adhesion

Our findings suggest that the osteoblasts attach to the rFN-coated titanium discs significantly higher than that found on the rVN-coated or untreated titanium discs. Compared with osteoblasts cultured on the rVN-modified titanium discs, osteoblasts that cultured on the rFN-modified titanium discs displayed better results in cell proliferation, MTS assay or ALP assessment. Consequently it can be concluded that the improved levels of cell proliferation, MTS assay or ALP activity on the rFN-coated titanium is due to its preference of titanium discs in protein adhesion rates, and thus suggests that surface chemistry-dependent protein adhesion rate ultimately may play important role in the degree of osseointegration.

PHASE COOPERATION OF METAL OXIDES IN VANADIUM-BASED MIXED OXIDE CATALYSTS FOR THE SELECTIVE OXIDATION OF HYDROGEN SULFIDE

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Hydrogen sulfide in the coke oven gas released from the steel smelting process is scrubbed and concentrated using aqueous ammonia solution. Concentrated H₂S that is separated from aqueous ammonia is transferred to the Claus plant to convert it into elemental sulfur, and remaining aqueous ammonia is usually incinerated. However, the separation of H₂S from the aqueous ammonia is not perfect and remaining aqueous ammonia stream contains about 2% H₂S which in turn causes the SO_x emission problem during the incineration. In this case, the control of SO_x emission is difficult because the stream contains not only excess water vapor but also high concentration of ammonia. One approach is the selective catalytic oxidation of H₂S to ammonium thiosulfate (ATS) and elemental sulfur as reported in our previous works. We reported a new vapor phase catalytic process for the selective conversion of H₂S.

In this study, we further examined the performance of vanadium-based mixed oxide catalysts for the selective oxidation of H₂S in the stream containing both of ammonia and water. The investigation was focused on the role of V₂O₅, and phase cooperation between V₂O₅ and other metal oxide such as Sb₂O₄ and Bi₂O₃. The deactivation of V₂O₅ catalyst was observed during the reaction, and the activity was recovered by the contact with oxygen. Strong synergistic phenomenon in catalytic activity was observed for the mechanically mixed catalysts of vanadium-based oxides and other metal oxide (Sb₂O₄ or Bi₂O₃). Temperature programmed reduction (TPR), oxidation (TPO), two separated-beds reaction test, and XPS analysis were carried out to explain the synergistic effect by the reoxidation ability of Sb₂O₄ and Bi₂O₃.

Poster OX-5

CONTROLLABLE GELATION OF HIGHLY CONCENTRATED NANO-SIZED COLLOIDS

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The high specific surface area and reactivity of nano silica particles makes highly concentrated suspensions susceptible to gelation in nonaqueous solvents. In this study, the gelation reaction of concentrated nano sized colloidal silica particles in a water-ethanol solvent has been controlled physicochemically with and without surface chemical modification. Thus, allowing the colloidal chemistry study of highly concentrated nano particle silica dispersions in nonaqueous solvents.

PREPARATION OF SILICA-COATED MAGNETIC NANOPARTICLES FUNCTIONALIZED WITH GLUCOSE

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The silica is well-known for the biocompatible material, and has the silanol groups at the end which make various ligands attach to its surface. So, the silica whose surface is functionalized with glucose can be applied to the biomedical techniques, for example, imaging techniques, because glucose is essentially required to the metabolism process. In addition, because of the magnetic nanoparticles which are embedded in silica particles, the collection of used nanocomposites is possible. Eventually, the purpose of this research is to prepare the silica-coated magnetic nanoparticles and functionalize them with glucose molecules.

The silica-coated magnetic nanoparticles are synthesized in two stages. First, Fe₃O₄ magnetic nanoparticles are made by co-precipitation method, which uses FeCl₂, FeCl₃ and base catalyst, NH₄OH. These particles have superparamagnetic behaviour, so the aggregation occurs spontaneously. To prevent them from aggregation, second stage is required. In second stage, we use sol-gel method to obtain silica-coated magnetic particles. TEOS is employed as the precursor material of silica. Because of high affinity between silica and magnetite surface, it is possible to encapsulate magnetic particles with silica directly. In this stage, ethanol and water are used as solvent, and the catalyst is NH₄OH. From the surface of Fe₃O₄ particles, the growth of the silica particles occurs and we can obtain magnetite-silica nanocomposites. After this process, silica particles in which a few magnetic particles are embedded have to be treated with the functional groups, for example, amine groups, to make the glucose molecules attach easily. Next, the glucose molecules are adsorbed to the silica surfaces by the interaction between amine groups of the silica surface and the hydroxide groups of the glucose.

The introduction of magnetic nanoparticles into the silica particles are confirmed by transmission electron microscope (TEM). Magnetic property of the products is measured by vibrating sample magnetometer (VSM). In order to test the chemical bonding between the silica and glucose, we use Infrared microscopy (IR).

EFFECT OF SURFACTANT ON SYNTHESIS OF TiO₂ HOLLOW MICROSPHERES VIA COLLOIDAL TEMPLATING

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Hollow TiO₂ microspheres were synthesized hydrothermally via the use of colloidal divinyl benzene spheres as a sacrificial template. The organic core particles of uniform shape and size were coated with layers of titanium bis(ammonium lactate) dihydroxide (TALH), and the effect of dispersants to the synthesized hollow spheres was examined. Hollow TiO₂ was verified by TEM and was formed regardless of the presence of dispersants. The yield for “good” hollow microspheres was nonetheless markedly different. When dispersant was not used, probability for the formation of broken hollow spheres was 1.55%. When nonionic dispersant TX-100 was used, the probability increased inversely to 2.19%. When anionic dispersant PSS was added, the probability was 1.6%. Finally, when cationic dispersant PDADMAC was used the probability reduced pronouncedly to 0.22%. This difference originates from the attainment of mono-dispersed colloid suspensions with reduced agglomeration so that uniform coating of TALH precursor can be made possible. Multiple coatings of PDADMAC/TALH on the template surface were also carried out. An increased shell thickness from 57 nm for the (PDADMAC/TALH)_{n=1} to 165 nm for the (PDADMAC/TALH)_{n=5}, where n denotes for the number of coatings, was found. The failure probability of broken hollow spheres was surprisingly 3.8% for the (PDADMAC/TALH)₅. This reveals that the coating layers need to provide a fugitive pathway for the decomposing organic core along with the simultaneous transformation to TiO₂ shell from the TALH upon thermal treatment.

EFFECT OF THE REACTANT-AOT COMPLEX ON PROPERTIES OF PARTICLES SYNTHESIZED BY AOT/ISOOCTANE/WATER SYSTEM

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Particles synthesized by W/O microemulsions have different properties compared to those formed by aqueous solutions.¹ This is because the microemulsions play a key role during the synthesis. However, the mechanism was not clarified in detail.

In order to investigate the effects of reactant-surfactant complex on particles properties, the syntheses of magnetite (Fe_3O_4) particles² were conducted using sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/isooctane/water system. The ratio of surfactant AOT and Fe ions was changed from 0.1 to 3.0. The aqueous solutions reaction was also carried out as a reference. The properties of the particles were characterized by a scanning electron microscopy (SEM), an X-ray diffraction (XRD), a vibrating sample magnetometry (VSM) and a Fourier transform infrared (FT-IR) spectroscopy.

Nano-particles of 10 to 30 nm are synthesized by the aqueous solutions reaction. The particle size enlarges with increasing the surfactant ratio for the AOT/isooctane/water system. Fe_3O_4 particles are synthesized by the aqueous solutions. The peaks of the Fe_3O_4 decrease with the surfactant ratio and change into the goethite (FeOOH) or amorphous. Amount of OH group in the synthesized particles are examined by a broad peak around 3400 cm^{-1} , an OH-stretching vibration band, of spectra obtained by the FT-IR. The particles synthesized by aqueous solution have almost no peak. On the other hand, the peak area enlarges with the surfactant ratio for the AOT/isooctane/water system.

A red precipitate of Fe-AOT complex was synthesized when the aqueous solutions of iron chlorides and AOT were mixed. The Fe-AOT complex was characterized by the FT-IR. The Fe-AOT complex has much OH-stretching vibration peak, indicating that the complex is hydrated. Due to this, the properties of particles synthesized by the AOT/isooctane/water system depended on the amount of the complex. This suggests that the reactant-surfactant complex such as Fe-AOT plays an important role to determine the properties of particles synthesized by W/O microemulsions.

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Poster DB-1

**ARRAYS OF MICROLENSSES WITH TUNABLE FOCAL LENGTHS
FABRICATED BY RESTRUCTURING POLYMER SURFACES WITH
AN INK-JET DEVICE**

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A method for fabricating two-dimensional arrays of polymer microlenses with tunable focal lengths between 0.2 and 4.5 mm is presented. We first make concave microlenses by ink-jetting solvent droplets on a polymer substrate with a standard, commercially available device. Solvent evaporation restructures the surface by a series of combined chemical and physical effects, which are discussed. In the second step we cast convex elastomeric microlenses with the template made in the first step.

We demonstrate the good optical quality of the microlenses by characterising their surfaces with atomic force microscopy and white light interferometry, and by directly measuring their focal lengths with ad-hoc confocal laser scanning microscopy.

A NEW BIO-PHYSICAL APPROACH TO UNDERSTANDING SELF-ASSEMBLY OF DAIRY PROTEINS

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The thermal processing of milk changes the composition and surface properties of the colloidal particles present and alters the physical properties of the milk. Whilst some changes such as those used to improve the texture of products such as yoghurt and are hence desirable, others such as gel formation during the manufacture of *Ultra-High Temperature* milk are highly undesirable. This work is part of a program to characterize the effects of milk composition on the chemical and physical changes that occur when milk is heated in order to understand and control the effect of thermal processing on the functional properties of the milk. Particularly important are :

- (i) the changes to the integrity of the casein micelles and the extent to which they are reversible,
- (ii) changes to the speciation of the components of the serum as they re-equilibrate in response to the changed environment.
- (iii) the denaturation of the whey proteins,
- (iv) the interaction between the components of the micelles and those in the milk serum, particularly those interactions that lead to aggregation or other changes that affect the functional properties of the milk,

Previous studies have been carried out by heating the milk, cooling it to room temperature and only then determining the changes that have occurred. This work is focused on the direct measurement of the changes as they occur in real time.

This paper presents some initial results of the study of the changes to the casein micelles on heating skim milk using normal and concentrated skim milk systems (pH = 6.2 – 7.2) at 90°C on pH (direct measurement), phosphate speciation (³¹P NMR) and pCa (change in solubility of CaHPO₄). The results show

- (i) that the decrease in pH on heating is correlated with the decrease in solubility of micellar calcium phosphate with increasing temperature, with the re-equilibration of H₂PO₄⁻ and HPO₄²⁻ (³¹P NMR), and with the concentration of the milk.
- (ii) that changes in pH and pCa are reversible on cooling but that re-equilibration is slow.
- (iii) that pH is an important parameter in controlling changes in viscosity on heating

These studies demonstrate that ³¹P NMR is a powerful tool for characterizing phosphate speciation at high temperatures.

ULTRASONIC ATTENUATION SIZING OF NANOEMULSIONS, MICROEMULSIONS AND POROUS PARTICLES

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Ultrasonic attenuation was used to size colloidal emulsion systems (oil in water, O/W, or water in oil, W/O) such as microemulsions, nano-emulsions and macro-emulsions as well as porous materials. Complementary dynamic mobility measurements enabled surface properties of the emulsions to be determined. Droplet sizes as low as 10 nm could be sized for the microemulsion system consisting of water-in-oil stabilised with AOT. Alkane emulsions stabilised with ionic or non-ionic surfactants were made and the sizes of the drops were between 30-400 nm. The increase in size with time due to Ostwald ripening was compared with the theoretical ripening rates.

Recent work on porous materials has also shown that such particles exhibit enhanced attenuation due to their porosity. The attenuation signal of a porous particle has a different shape and magnitude than that predicted by viscous attenuation alone (Fig. 1). O'Brien¹ has shown that the attenuation signal of a porous particle depends on the pressure diffusivity and porosity. Preliminary results on selected porous materials support the theory².

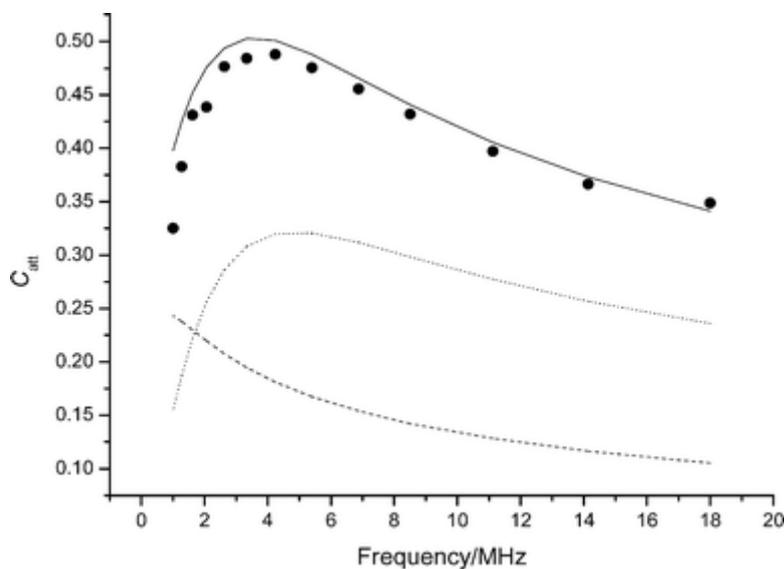


Fig. 1 Experimental (●) and theoretical ultrasonic attenuation spectra for Platinum™ silica. Theoretical data: (- - -) viscous attenuation; (···) porous attenuation; solid line total attenuation (viscous + porous). Hydrated particle weight fraction 0.103; hydrated particle density 1.85 g cm⁻³; porosity 0.29; pressure diffusivity 0.025 cm² s⁻¹; d_{50} 2.0 μm, d_{85} 2.4 μm.

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NEW EMULSIFYING AGENTS FOR FOOD APPLICATIONS

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This study concerned with the development of new emulsifying agents which can be used as food additives. Previous work has shown that surfactants formed by the conjugation of proteins with polysaccharides give enhanced stabilization of oil in water emulsions with the protein being absorbed onto the surface of the oil droplet and the hydrophilic polysaccharide providing enhanced steric stabilization. In addition conjugates have been proven to have low toxicity and to be thermally stable such that they can be used as ingredients where the material will be cooked. Whilst there has been a considerable amount of work using conjugates between polysaccharides and the proteins β -lactoglobulin and lysozyme there have been few studies using the caseins

The focus of this work is to prepare and investigate the properties of sodium caseinate – dextran conjugates formed by the Maillard reaction (reaction between a reducing sugar at the end of a polysaccharide chain and a free amino residue on the protein). The caseins were chosen because of their lack of quaternary structure, their low cost and their current use as food ingredients the dextrans are available in a range of molecular weights. The caseins possess a number of free amino groups giving rise to possibility of a comb type structure with a hydrophobic spine and hydrophilic teeth.

Surfactants were prepared using dextrans of three different sizes. They were characterised chemically and their surface activities relative to β -casein determined. The surface behaviours studied included adsorption and interfacial tension studies at the air/water and oil/water interfaces, adsorption onto polystyrene lattices and their performance as emulsifiers when used to prepare vegetable oil in water emulsions.

Poster DB-5

THERMOCAPILLARY MIGRATION OF A FLUID DROP PERPENDICULAR TO TWO PLANE WALLS

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The quasi-steady problem of the thermocapillary motion of a spherical fluid drop situated at an arbitrary position between two infinite parallel plane walls is studied theoretically in the limit of negligible Marangoni and Reynolds numbers. The applied temperature gradient is constant and normal to the plane walls. The presence of the plane walls causes two basic effects on the drop velocity: first, the local temperature gradient on the drop surface is altered by the walls, thereby speeding up or slowing down the drop; secondly, the walls increase viscous retardation of the moving drop.

To solve the thermal and hydrodynamic governing equations, the general solutions are constructed from the fundamental solutions in both cylindrical and spherical coordinates. The boundary conditions are enforced first at the plane walls by the Hankel transforms and then on the drop surface by a collocation technique. Numerical results for the thermocapillary migration velocity of the drop relative to that under identical conditions in an unbounded medium are presented for various values of the relative viscosity and thermal conductivity of the drop as well as the relative separation distances between the drop and the confining walls.

The collocation results agree well with the approximate analytical solutions obtained by using a method of reflections. The presence of the walls always reduces the drop velocity, irrespective of the relative transport properties of the drop or the relative drop-wall separation distances. The boundary effect on thermocapillary motion of a drop normal to two plane walls, which is relatively weak in comparison with the corresponding effect on sedimentation, is found to be quite significant and generally stronger than that parallel to the plane walls.

Poster DB-6

INFLUENCE OF GAS TYPE ON BUBBLE RISE VELOCITY – IMPLICATIONS FOR INTERFACIAL BEHAVIOUR

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The process by which a gas bubble attaches to a hydrophobic surface in an aqueous phase is of great importance in froth flotation, heavily utilised in the mineral processing industry to concentrate pulverised ores on the basis of differential hydrophobicity. The accurate modelling of flotation efficiency, based on individual particle-bubble interactions is of key interest in flotation research. These bubble-particle interaction models require a knowledge of the hydrodynamic state of the bubble surface. In the present study, single, clean, gas bubbles of N₂, He, CO₂ and air, with diameters ranging upwards from 10µm were produced in extremely clean water. Terminal rise velocities were measured by video-microscopy and the data obtained compared with models for terminal velocity. It was found that even the smallest bubbles of each gas had rise velocities following the Hadamard-Rybczynski model, indicating a completely mobile surface, down to 10µm bubble diameters. The terminal velocities of very small bubbles (10-40µm) exceeded the maxima predicted by the Hadamard-Rybczynski equation, with a more significant deviation shown by air and CO₂ bubbles. A dependency on gas solubility is evident, which is linked to the nature of the gas-water interface. This will influence the attachment of particles and bubbles.

PHYSICAL PROPERTIES OF PHASE CHANGE NANOEMULSIONS

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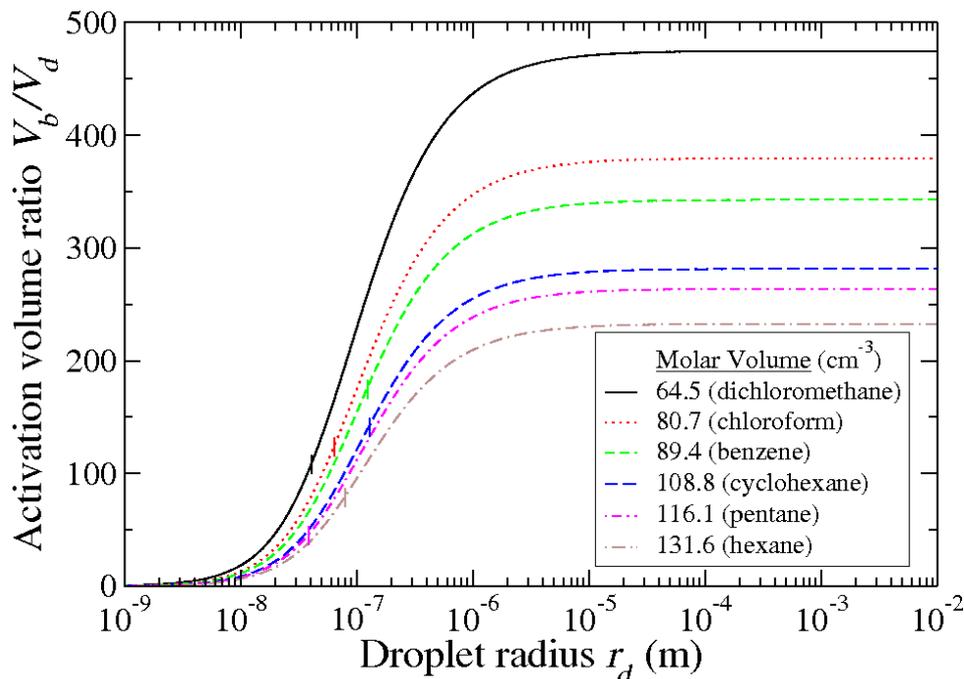
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Liquid-gas and liquid-solid phase change emulsions find application industrially as thermal exchange materials due to their high heat capacities, but applications have been suggested in other areas such as ultrasonic imaging. These applications have focused on microemulsions with droplets larger than $10\mu\text{m}$ in size where the effect of the phase change is the same over all droplet sizes.

In liquid-gas phase change nanoemulsions with droplets smaller than $1\mu\text{m}$ the droplet's increasingly large Laplace pressure becomes significant in determining the size of the resulting gas bubbles produced by the phase change, with the ratio of gas bubble size to liquid droplet size falling as the droplet radius decreases.

The difference in solubility of droplet material before and after the phase change is also strongly affected by droplet size. When solubility equilibration of material dissolved in the bulk phase out of the gas bubbles is slow enough to allow the equilibrating gas bubble size to be measured, then an estimate of the system's diffusion constant may be calculated.

When the droplets are sufficiently small then after phase change all the material from the gas bubbles is dissolved into the bulk phase. We suggest this phenomenon may be used in the construction of nanostructures where the nanoparticle material may be carried in the liquid droplets and the droplet material then being extracted via small droplet phase change.



MICROFLUIDIC PROCESSING OF MULTIPHASE FLUIDS

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Microfluidics offers many advantages over conventional chemical and biological processing, particularly concerning minute (rare or valuable) sample volumes, minimal waste production, mixing and reaction kinetics, high throughput and online analysis. In recent years, much attention has been directed towards “discrete” microfluidics, where liquid samples are transported in discrete packets (droplets), rather than continuous flow.

The discrete approach to microfluidics constitutes three essential components: droplet generation, droplet manipulation and controlled coalescence. In our research, we have studied the generation of monodisperse emulsions at high dispersed volume fractions, *i.e.* gel emulsions. Monodisperse gel emulsions self-organize into highly ordered foam-like arrangements, which facilitate droplet positioning for targeted coalescence using low-voltage applied potentials, *i.e.* electrocoalescence. We show that electrocoalescence proceeds *via* an electric-field-induced dynamic instability in a fraction of a millisecond. When electrode geometry and applied potential are optimized, individual lamellae can be targeted for rupture within highly ordered droplet arrangements.

Although ideal for many samples, discrete microfluidics exhibits problems inherent in processing complex fluids. In microchannels, adsorption of particles or biomaterial (*e.g.* proteins) can lead to cross-contamination or complete obstruction of channels, *e.g.* prior to droplet formation. Consequently, our present work is addressing the influence of the channel’s surface properties (wettability, roughness, and electrical double-layer) on microchannel fouling.

Poster DB-9

**HYDRODYNAMIC INTERACTIONS BETWEEN A SILICA PARTICLE
AND A DEFORMABLE DROPLET – EFFECT OF
PARTICLE/DROPLET SIZE RATIO AND BULK PHASE VISCOSITY**

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In many industrial applications such as froth flotation, foams and emulsions, the interactions between solid and deformable interfaces, or two deformable interfaces, is of critical importance. Understanding these micro-scale interactions is vital for the prediction and control of the macro-scale behaviour. Recent advances within the PFPC has enabled the modeling of atomic force microscope (AFM) force data collected for the dynamic interaction between a solid sphere and a deformable interface¹. Here we present data examining the effect of the particle/droplet size ratio and the bulk phase solution viscosity on the interaction between silica spheres and tetradecane droplets. In particular, this data enables us to probe the existence, or otherwise, of a slip boundary between the two interacting surfaces. Force-distance profiles collected from AFM experiments are compared to theoretical profiles in which different slip lengths are incorporated.

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**IN SITU DETERMINATION OF THE SIZE AND POLYDISPERSITY OF
CONCENTRATED EMULSIONS**

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Many physical properties of emulsions are affected by the drop size distribution, including stability to coalescence and gravity-induced separation, flow and deformation behaviour, visual appearance, texture and flavour. The accuracy of most techniques currently used to size emulsion drops is limited for highly concentrated, polydisperse, or marginally stable emulsions. We measured the droplet size distributions of concentrated, polydisperse oil-in-water emulsions using a novel combination of Ultra Small Angle Neutron Scattering (USANS) and electroacoustics. The mean radii calculated by fitting a model for polydisperse hard spheres with excluded volume interactions to the USANS data were consistent with those derived from electroacoustics on diluted emulsions after correction for conductance behind the shear plane. The Porod radii measured by USANS were similarly consistent with the mean surface area weighted radii derived from electroacoustics, irrespective of the drop concentration or polydispersity.

TWO-DIMENSIONAL MONTE CARLO SIMULATIONS OF SELF-ASSEMBLY CLUSTERS COMPOSED OF ROD-LIKE FERROMAGNETIC PARTICLES

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Self-assembly has received considerable attention recently as an important method for a hierarchical structure design. Colloidal particles can also form the self-assembly structures in nano scale so that the structures can be applied to make nanomaterials, such as photonic crystals and well-arranged quantum dots.

We have been studied theoretically on self-assembly structures of ferromagnetic particles in suspensions because the particles can be controlled by an external magnetic field. In this study we focus our attention on the self-assembly clusters composed of rod-like ferromagnetic particles because formation of a new basic structure, that is, anti-parallel particle pairs can be predicted to form from the energetic point of view. Hence, wide varieties of self-assembly structures are expected to be found.

A ferromagnetic rod-like particle is idealized as a spherocylinder. The particle has magnetic charges $\pm q$ at the center of each hemisphere and is covered with a surfactant layer. We conducted the cluster-moving Monte Carlo simulations for different values of the dimensionless parameters for the particle-particle interactions, the aspect ratios and the particle-field interactions, respectively. The internal microstructures obtained by simulations were analyzed in terms of orientational distribution functions, pair correlation functions and radial distribution functions. In addition, the cluster size distributions have been investigated.

The results show that as the magnetic interaction between particles increases, many small clusters such as anti-parallel particle pairs, raft-like clusters, and small loop-like clusters are formed; these gather to form larger aggregates. In the case of a relatively strong magnetic interaction between particles, solid-like rectangular clusters are formed (**Figure**) when the aspect ratio is approximately 2, since the suitable distance between magnetic charges enables particles to form a fundamental cluster of two normal anti-parallel particle pairs. As the aspect ratio increases beyond 2, many more stable raft-like clusters are formed, since the increase in distance between magnetic charges makes the two normal anti-parallel particle pair structures unstable. For a significantly larger aspect ratio, large network microstructures are produced by the formation of many chain-like and loop-like structures.

As the magnetic field increases, particles align to the magnetic field direction. In the case of a relatively strong magnetic interaction between particles, chain-like clusters are formed along the magnetic field direction. Two types of structures in the chain-like clusters are observed, such as a straight linear structure and a step-like structure. The step-like structure formation can be explained by the dependence of the potential energy curves on the shape of a spherocylinder particle.

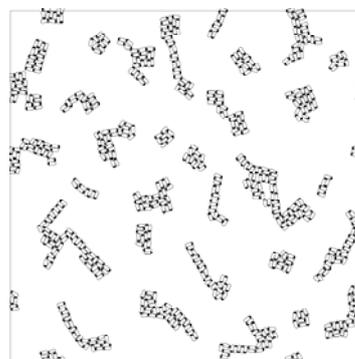


Figure Self-assembly clusters of ferromagnetic rod-like particles

ADSORPTION OF LIQUID CRYSTALLINE PARTICLES AT SURFACES

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Introduction. Nanostructured, non-lamellar self-assembled systems such as cubic and hexagonal phase liquid crystals, are generating substantial interest in the pharmaceutical industry due to their potential to incorporate actives of varying physicochemical properties and to provide sustained release. In some circumstances, the bulk liquid crystalline structure may be dispersed to form submicron particles (eg. cubosomes and hexosomes), which retain the internal bulk phase structure. Whilst the internal nanostructure of the bulk and dispersed liquid crystalline phases are well characterized, there is no information on how the adsorption of liquid crystalline particles at surfaces depends on the composition or internal nanostructure. Our previous investigation (published) indicated that, unlike GMO-based cubosomes, phytantriol-based cubosomes and hexosomes do not change their lattice structure with addition of Pluronic F127 block co-polymer as stabilizer. These findings lead to the hypothesis that F127 stabilises the GMO and phytantriol-based cubosomes and hexosomes in very different ways and that this may influence the interaction of these particles with surfaces.

Methods. The spontaneous adsorption of dispersed cubosomes and hexosomes based on phytantriol and GMO at hydrophilic / hydrophobic surfaces were studied using ATR-FTIR and adsorption rates modeled using Langmuir adsorption isotherms. The adhesion properties of liquid crystalline surface were investigated further using AFM in excess water with hydrophobic and hydrophilic tips and in the presence and absence of F127.

Results. Phytantriol-based cubosomes showed a higher adsorption rate at hydrophobic surfaces than hydrophilic surfaces, whilst the phytantriol-based hexosomes and GMO-based cubosomes did not show this discrimination. Desorption of GMO cubosomes induced by solution agitation indicated a weaker force of surface adsorption than phytantriol-based cubosome and hexosomes. AFM experiments in the absence of F127 revealed a stronger adhesion force for liquid crystalline surfaces with hydrophobic probes than with hydrophilic probes. F127 addition to GMO-based cubic phase induced a significant reduction in adhesion force whilst it had minimal effects on phytantriol-based cubic phase. Phytantriol-based hexagonal phase showed an increase in adhesion force and prolonged force hysteresis during approach and withdraw of the probes in the presence of F127.

Conclusion. Although F127 is used to stabilize GMO and phytantriol-based liquid crystalline dispersions, the specific mechanism of interaction between F127 and the liquid crystalline dispersed particles differs, affecting the mode of adsorption particle characteristics on solid surfaces. A correlation was found between cubosome and hexosome adsorption behaviour, and the force of interaction between the parent liquid crystalline surface and hydrophobic and hydrophilic probes in the absence and presence of F127 stabilizer.

THE PHASE BEHAVIOUR OF STRAIGHT AND BRANCHED UREA BASED SURFACTANT MIXTURES

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Mixtures of different surfactants often alter the physicochemical properties of the pure surfactant and thus generate new types of aggregates. The initial hypothesis for this mixture study was that, by mixing two surfactants, where one is a straight chain urea surfactant without highly ordered liquid crystalline phase, with another isoprenoid type branched urea surfactant demonstrating hexagonal liquid crystalline phase, the mean curvature and the Critical Packing Parameter (CPP) value could be ameliorated in order to favour the formation of other interesting lyotropic liquid crystalline phases. Using differential scanning calorimetry (DSC) and microscopy with crossed polarizers, this study examined the thermal and lyotropic behaviour of, two isoprenoid branched urea surfactants, hydroxyfarnesyl urea (HFU) and phytanyl urea (PU), with addition of corresponding straight chain urea surfactant.

In both pairs of mixtures, adding straight chain urea surfactants dramatically increased the thermal phase transition temperature and enthalpy. In the mixtures in which straight chain composition were less than 40%, the glass transition was maintained in both mixture systems. For the higher composition mixtures (straight chain composition >50%), however, only a single large melting peak existed. Self-assembled structures of these mixed surfactants in water exhibited lamellar and/or hexagonal phase within the lower composition range of straight chain surfactant, and crystalline phase within the higher composition region. These results indicate that the physicochemical properties of these mixtures are mainly dependent upon the composition of the mixture.

Poster HM-4

NANOMECHANICAL TESTING AND MODELING OF NATIVE COLLAGEN FIBRILS

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Animal connective tissues and the extracellular matrix are comprised of almost-crystalline collagen fibrils in discretized random-array networks or as hierarchical macrostructures. The fundamental basis for this set of polymers is the tropocollagen molecule but the primary structural unit is the fibril. Study of the fibril is hindered by the lack suitable isolation strategies and incomplete understanding in the effects of collagen-affiliated proteoglycans to *in vivo* precipitation. Using readily extractable fibril moiety analogous to type I, we present herein nanomechanical testing of native, precipitated *in vivo*, adult collagen fibrils. Nanomechanical testing via radial indentation and nanoscale three point bending was performed under ambient and physiological conditions demonstrating a material anisotropy in both conditions without sheer effects; and we illustrate a suitable mathematical model relating the elasticity of fibrils to a semi-braided monomer/micro-fibril model. The model was inverted to extract the modulus expected for the tropocollagen molecule which is in agreement with X-ray and theoretical modeling. We hypothesize internal fluid density provides the mechanisms for fibril elasticity based molecule alignment to the director with little tension induced extension at low strains.

INK-JET PRINTING OF NOBLE METAL NANO-COLLOIDS PREPARED BY POLYOL PROCESS

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Ink-jet printing is a non-contact technique of imaging computer data by means of jetting the ink from a small orifice to a specified position on a substrate. This technique has the advantage of being a fast, simple, low-cost and high-throughput technology. Thus, ink-jet printing technique has been successfully used in the last decade for many applications, such as OLED, transistor and integrated circuits, conducting polymer devices and biomolecular arrays. It is very important to optimize the physicochemical properties of the inks (viscosity, surface tension, adhesion to a substrate and etc.) in order to achieve optimal performance and reliability of the printing system and to obtain the best printed pattern.

In this study, noble metal nanoparticles such as Ag, Au and Pt were deposited on PET film by ink-jet printing technique using piezo-based EPSON desktop ink-jet printer (Stylus C67). Noble metal nano-colloids were prepared by polyol process in the presence of poly(vinyl pyrrolidone). The viscosities and surface tensions of the metallic inks were adjusted through the mixture of solvents and the surfactants. The patterns were designed by Power Point 2003. The amount of the inks deposited on the PET film was controlled by 'luminosity' (L) value in the HSL (hue, saturation, luminosity) function.

Surface morphology and roughness of the metal-printed film were investigated by SEM and AFM. Optical properties of the patterned films were observed by UV-vis spectra..

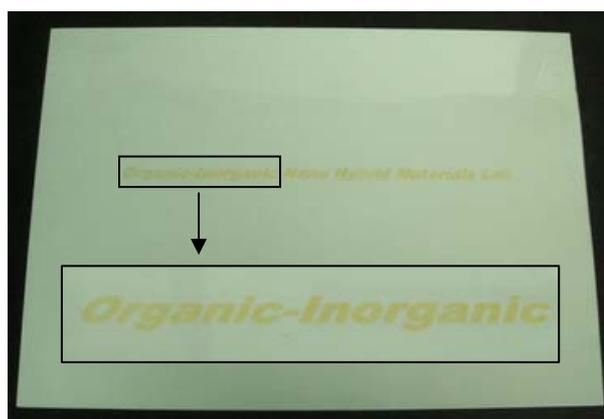


Figure. Patterns printed on PET film using Ag nano-colloid with EPSON Stylus C67 DeskJet printer

ASSEMBLY OF NANOSTRUCTURED $\text{Li}_4\text{Ti}_5\text{O}_{12}$

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As technology grows at a rapid rate, more powerful energy storage devices are necessary to accommodate the ever-increasing energy requirement. Improvement on a battery's performance can be made by optimising its electrode properties. In this study lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is chosen because it has unique features that make it very attractive as a potential negative electrode in lithium ion batteries e.g. flat operating voltage during charge-discharge cycles, and negligible capacity fading.

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 a 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.

The aim of this study is to control the crystallinity and porosity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and investigate how this influences its electrochemical properties. Results showed that both the crystallinity and porosity are highly dependent on the synthesis process. In addition, the use of surfactants to achieve finer control the porosity was also studied.

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PROTIC IONIC LIQUIDS AND THEIR POTENTIAL APPLICATIONS

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Protic ionic liquids (PILs) are a subset of ionic liquids formed by proton transfer from a Bronsted acid to a Bronsted base. Some characteristic features of PILs are their ability to form H-bonds and mediate hydrocarbon-solvent interactions. PILs have been investigated as amphiphile self-assembly media, biological solvents and in polymer membrane fuel cells. We recently studied the phase behaviour and the physico-chemical properties of a large number of PILs containing the primary ammonium cation with either a carboxylate organic anion or an inorganic anion. Studies are underway to explore the potential applications of these PILs as self-assembly media, solvents for protein stabilization and in energy storage devices.

DEVELOPMENT OF A POLYVALENT INHIBITOR OF CHOLERA TOXIN USING A BIO-FUNCTIONALISED SURFACTANT MESOPHASE

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The polyvalent interaction between multiple carbohydrate moieties and protein receptor molecules plays an essential role in the recognition of plant or bacterial toxins with the host cell surface [1]. The development of receptor-binding antagonists that mimic the multiple carbohydrate–toxin protein interaction and block cell surface recognition is an attractive approach to the development of novel prophylactics or therapeutics. Lyotropic mesophases, resulting from the self-assembly of surfactant molecules into highly ordered liquid crystalline phases, provide excellent 3-D nanostructured scaffolds for the presentation of high densities of ligand molecules [2]. We have found that a cubic lyotropic mesophase comprised of a mixture of the surfactant amphiphile phytantriol with the ganglioside G_{M1} , efficiently bind cholera toxin (CT), the causative agent of cholera, in a polyvalent interaction. Surfactant systems containing up to 20% G_{M1} / phytantriol afforded a hydrated insoluble gel-like material, which retained an inverse cubic phase (Q) structure in excess water and at physiological temperature. The G_{M1} -functionalized mesophases removed up to 98.8 % of CT from solution containing between 6.25 and 100 ng/mL of CT with a dissociation constant (K_d) of 0.12 nM. The inhibitory effect of the mesophases is enhanced by the surface mobility of G_{M1} within the scaffold, which facilitates precise pattern matching of the G_{M1} groups with the binding epitopes on the toxin surface. The lateral mobility of the G_{M1} in the mesophase ameliorates the requirement for the incorporation of precise structural features (based on toxin crystallographic data) in toxin inhibitor design. This approach provides a new route to a unique class of polyvalent inhibitors, which should be broadly applicable to a range of bacterial and plant toxins.

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**NONIONIC AMIDE AND MONOETHANOLAMIDE SURFACTANTS
WITH ISOPRENOID-TYPE HYDROCARBON CHAINS:
THERMOTROPIC AND LYOTROPIC LIQUID CRYSTALLINE PHASE
BEHAVIOUR**

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Lyotropic liquid crystalline phases (in particular cubosomes and hexosomes) formed from aqueous surfactant systems have been shown to provide ideal matrices for sustained drug release. In the development of a self assembling drug delivery system, it is important that the system be biocompatible, that it forms inverse hexagonal and/or cubic phases that are stable in the presence of excess water, and that these phases form at physiologically relevant temperatures. Due to these constraints, the choice of suitable surfactants has been limited.

A family of naturally occurring amphiphilic molecules (fatty acid ethanolamides) make ideal self assembling drug delivery systems due to the fact that they exhibit interesting biological and medicinal properties. In addition, they are ideal candidates for forming inverse phases in that they consist of a small ethanolamide head group and highly cis-kinked hydrophobes giving them the desired reverse wedge shape. We have developed a series of surfactants based on the structure of these naturally occurring amphiphiles which possess an ethanolamide head group and hydrophobic chains of varying lengths. Analogous amide surfactants were also examined. We investigated the thermotropic and lyotropic liquid crystalline phase behaviour of these surfactants.

The amide surfactants had higher melting points than their ethanolamide counterparts. In addition, the melting points decreased for both surfactant groups with increasing chain length. Interestingly, the two longer chained ethanolamide surfactants both possess glass transition temperatures at ~ -72 to -73°C . The amide surfactants and the short chained ethanolamide surfactant all showed only one isotropic phase that formed at the water/neat surfactant interface, this phase was quite fluid and most likely corresponds to an L2 phase.

However, both of the longer chained ethanolamide surfactants displayed very interesting phase behaviour. One showed two isotropic phases that became one with increasing temperature and finally turned into an isotropic melt. With the second, two isotropic phases were also initially present. With increasing temperature one of these isotropic phases turned into a hexagonal phases, and with further increases in temperature the second eventually disappeared and finally the whole system became an isotropic melt. Moreover, these phases formed within a physiologically relevant temperature range. In addition, drug delivery vehicles were prepared from the bulk phases of these two surfactants. Cryo-TEM showed particles with definitive internal pore structure, and FFT analysis indicated either hexagonal or cubic structure. Thus, these latter two surfactants are ideal candidates for drug delivery applications.

PREPARATION AND CHARACTERIZATION OF ZSM-5 OF HIERARCHICAL PORE STRUCTURES

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Zeolites are useful for a variety of applications, for example, heterogeneous catalysis, adsorption, and separation and purification. Although synthesis, characterization, and applications of zeolites are well-developed, micropores of the molecular size range of 0.3 to ~1.5 nm in zeolites often impose diffusion limits on the reaction rate and cause high back pressure on flow systems. Here we present the detailed preparation and characterization of hierarchical ZSM-5 zeolites of mesopore-containing regular structures, which are either prepared by template-synthesis method with carbon aerogels and resorcinol-formaldehyde aerogels as templates or alkaline post-treatment. The samples were characterized with respect to their pore structures and chemical structures by means of nitrogen adsorption at 77 K, field emission scanning electron microscopy, thermogravimetric analysis, X-ray diffraction, FT-IR spectroscopy, ²⁹Si nuclear magnetic resonance spectroscopy, and X-ray photoelectron spectroscopy.

Experimental results show that the materials from template-synthesis consist of three-dimensional mesopores, and the mesoporous systems can be influenced by proper preparation of resorcinol-formaldehyde aerogels and carbon aerogels through solution chemistry. While alkaline post-treatment develops mesopores which are introduced mainly from the boundary portion of MFI zeolites to the bulk; the alkaline treatment periods have influence on the developments and structures of mesopores. Since crystallinities and short-range order in zeolites of hierarchical pore structures have remained virtually unchanged, and the modified mesoporosities are beneficial to easier transport of guest molecules and products, these materials could be useful as potential heterogeneous catalysis for bulkier molecules where diffusion of reactant molecules could be facilitated.

POLYELECTROLYTE-STABILIZED LIQUID CRYSTAL DROPLETS AS NANO-SENSORS

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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.

This work centres on using the layer-by-layer (LbL) technique to deposit polyelectrolyte multilayer films at interfaces between liquid crystals and aqueous phases.¹ 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.

One advantage of the LbL method is that it is also applicable to colloids. We have recently found that the nematic liquid crystal 5CB can be emulsified with water to form small droplets. When 5CB is emulsified with a charged lipid or a polyelectrolyte, a charged interface is formed on which multilayer films can be assembled. In addition, the multilayer coating could mediate the interactions between the liquid crystals and different analytes, thus providing a novel way to distinguish between different analytes.² The stability of the multilayers was confirmed by the formation of stable hollow capsules upon dissolution of the liquid crystal core. These results are significant in that (a) they demonstrate the ability to prepare stable liquid crystal emulsions with an easily modifiable interface, and (b) they show that emulsions can be used to template polyelectrolyte multilayer formation. These systems can be engineered to turn the droplets into sensors.

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COMBINING SELF ASSEMBLY WITH LITHOGRAPHY TO FABRICATE 3D PHOTONIC CRYSTALS, FUNCTIONAL DEVICES, AND NANOSTRUCTURES

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Self assembly of colloidal microspheres produces many interesting structures, which can be used as templates or masks to fabricate more advanced structures and devices. For example, photonic crystals (PCs, also known as photonic bandgap materials), a semiconductor for light, can be fabricated using self-assembled colloidal crystals as templates. This presentation discusses our recent research results on fabrication of three-dimensional PCs, functional defects embedded in 3D PCs, and nanostructures based on self-assembled colloidal crystals, together with the assistance other materials processing techniques. It begins with a demonstration of how the self-assembly method alone can be used to fabricate planar defects, followed by how self assembly is combined with nanolithography to fabricate complicated defects, including line, point and planar defects. Then, it discusses how self-assembled monolayer can be used to fabricate various nanostructures and functional materials.

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Poster FR-1

INVESTIGATION OF POLYSACCHARIDES ADSORBED ON MOLYBDENITE

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Molybdenite (molybdenum disulfide MoS_2) is a naturally hydrophobic trace mineral encountered in complex sulphide ores. Due to high price of molybdenum, mining companies are particularly interested in improving recovery and grade in molybdenite circuits. Polymers are often used as depressants to inhibit the recovery of other minerals by decreasing their hydrophobicity. However, most polymers also affect the flotation behaviour of molybdenite.

The purpose of this study is to investigate how the properties of an adsorbed polymer layer might impact on the recovery of molybdenite during the flotation process. The adsorption of a range of polysaccharides on cleaved atomically flat molybdenite has been studied using in and ex-situ AFM imaging, sessile drop and captive bubble contact angle measurements. In addition, adsorption isotherms and Washburn contact angle determination have been performed for polymer treated molybdenite particles. The results of these studies have allowed us to correlate surface coverage, layer thickness and roughness with the ability of the polymer to reduce the wettability of molybdenite.

A complementary study of polysaccharides adsorbed on other hydrophobic minerals such as talc and graphite is under investigation.

QUANTITATIVE MEASUREMENT OF PHOTON PRESSURE USING FM RESOLUTION AFM

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A technique is described where the pressure exerted by a laser beam, known as photon pressure, which fully illuminates the lower surface of a microcantilever is quantitatively measured. This technique is based upon the Atomic Force Microscope (AFM) and represents the first quantitative measurement of photon pressure using a cantilever beam. The exerted pressure arises from the conservation of momentum when the photons are reflected and absorbed by the cantilever. The resolution of the measurement of the cantilevers deflection is approximately 0.3pm. This highly sensitive technique has a broad range of applicability to observing weak chemical and biological interactions acting over short length scales. An example of how photon pressure can be used to accurately control the motion of the cantilever will be presented.

CRYSTALLIZATION IN THE PRESENCE OF DYNAMICAL ARREST

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In recent years there have been concerted efforts to understand the phenomenon of 'dynamical arrest', that process in which many particles dramatically slow in a concerted manner. There have been efforts to describe dynamics using dynamically available volume, starting some years ago, and more recently a growing understanding of the connection between available space and dynamics has begun to emerge.

Understanding the manner in which ordered structures grow in the vicinity of dynamical arrest is one of the more pressing and important questions in modern condensed matter science. In recent years, nanoscience has focussed greatly on the creation of increasingly small and more functional particles, and devoted proportionately less attention to rational approaches to assembling structures from them. On the other hand, it has increasingly been realized that useful devices will require us to fabricate ordered structures from these particles, and in the longer term it will be necessary to approach this questions in a fundamental manner.

A possible theoretical approach could be to seek a general understanding, perhaps even paradigms, for the principles governing ordering in nearly arrested systems. In particular we would like to see how ordering phenomena are controlled by the numbers and heights of barriers (on all length scales) originating from the caging (and related effects) that drive dynamical arrest. Also, in repulsive systems it is desirable to understand how (rare) empty space is managed in the process of forming ordered structures. This would extend existing knowledge about dynamically available volume to non-equilibrium systems. In turn this could help to clarify how locally (and globally) available volume controls the nature and quality of 'ordered' structures, perhaps informing future studies on the detailed particle design required to avoid the worst bottlenecks in reaching equilibrium.

Simple lattice models could be of great value, being simple and efficient to explore, and yielding a general overview (though not detail) rapidly with a high degree of confidence. Here we introduce the first such model, and set it in the context of previous related ideas. It is a simple model, possessing both crystal and glass transition and unifying different approaches without loss of the simplicity that theorists require. Within the model we calculate equilibrium phase diagrams, energy relaxation, structure factor and other classical signatures. We suggest that this model can also be applied to other interesting questions such as nucleation and fibrillation of proteins.

DETERMINATION OF NANOSIZED SiO₂ PARTICLE CONTACT ANGLES, VIA MULTIANGLE, SINGLE WAVELENGTH ELLIPSOMETRY

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The accurate determination of nanoparticle contact angles is an area of great attention in engineering industry and scientific fields, because of both the practical complexities and importance of categorising such information. In absolute terms, no particle smaller than the wavelength of light can be resolved by visible microscopy, so no observational information on contact angle is possible (in real terms, great difficulty is had resolving visual information on much larger particles, up to 10 μ m). Hence work was completed to look at the use of Ellipsometry to indirectly categorise particle behaviour, specifically air-water contact angle.

Ellipsometry is a technique of interest, because it is non destructive, non-intrusive, and can be used to calculate both optical and structural properties (i.e. refractive index & thickness) of a given material. Ellipsometry has been used for many years to categorise various thin films and substrates with mainly 'homogenous' compositions. Its use to categorise layers of spherical particles is a more complicated proposal. A model was developed to associate a compressed layer of 270nm silica particles on water (both hydrophobic and hydrophilic) as a bi-layer system. The upper layer was associated as a mixture of silica and air, and the lower layer a mixture of silica and water. Using a Bruggeman Effective Medium Approximation, 'ideal' refractive indexes (N_1 , N_2) were calculated for both layers, for different silica immersion depths (i.e. increasing upper layer thickness T_1); considering the particle layer as a perfect spherical monolayer.

Ellipsometry data (DELTA and PSI plots) were gained over an angle of incidence range from 48-58° and wavelength 532nm. The raw data was resolved for its underlying information under the two layer model. The data was solved for incremental constant values of the upper layer (or a T_1 thickness relating directly to the non-immersed silica portion) and corresponding 'ideal' N values. An error analysis was completed, to determine the T_1 thickness related to the absolute minimum error (or the absolute solution thickness). This was associated directly as the height of the particles in air, and contact angle calculated. To further verify results, combined T_1+T_2 thickness data was compared to the diameter of the particles measured from light scattering techniques.

Preliminary results with uncleaned 'nominally' hydrophilic silica, gave contact angles of 35° \pm 2°. Combined thickness values equalled 250nm \pm 5nm, which compares reasonably to the light scattering size data.

SURFACTANT-BASED SEPARATION TECHNIQUE IN THE REMOVAL OF DISSOLVED ORGANICS FROM WATER

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Separation techniques based on the use of surfactants have several important advantages over traditional separation methods. Aqueous solutions of certain surfactant micelles exhibit phase separation behaviour upon temperature alteration. This phenomenon can be exploited in separation science for the development of extraction, purification and pre-concentration schemes for different solutes. Since the addition of just a small amount of an appropriate nonionic surfactant to the aqueous sample solution is required, this approach is convenient and fairly benign, eliminating the need for the use of organic solvents as in conventional liquid-liquid or solid-liquid extraction.

The technique of extracting dissolved species from water via nonionic surfactant micelle-mediated phase separation was studied. The effect on extraction efficiency, solute distribution coefficient and phase volume ratio of pertinent experimental parameters such as surfactant hydrophilicity, temperature and additives was systematically evaluated. Surfactant hydrophilicity was examined by monitoring the extraction parameters for two members of the homologous series of octylphenoxy polyethoxyethanols with varying ethylene oxide units.

The cloud point technique was used to recover phenol, o-chlorophenol and o-nitrophenol from aqueous solutions using octylphenoxy polyethoxyethanol as the nonionic surfactant. The experiments indicate that increase in temperature resulted in increased recovery of the solutes. Recovery of phenols follows the order of o-nitrophenol > o-chlorophenol > phenol and is increased in the presence of sodium chloride; a salting-out electrolyte. The presence of salting-out electrolytes is preferred both to decrease the cloud point and to increase the efficiency of extraction. It was also observed that as the surfactant hydrophilicity increases, the solute distribution coefficient decreased for all the solutes studied.

Poster FR-6

MIXED SYSTEMS OF CATIONIC - NONIONIC SURFACTANT SYSTEMS IN WATER

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Mixed surfactant systems have many practical applications compared to single surfactant. Out of several possibilities we have studied mixed surfactant systems of cationic surfactants and nonionic surfactants e.g. alkyl pyridinium halides (C_nPyX , $n = 12, 14, 16$ and $X = Cl, Br, I$) with dodecyl polyoxyethylene ethers, $C_{12}E_m$, ($m = 9, 10, 12, 15$) in aqueous solution at their different mole fraction (0-1). Apart from classical techniques like surface tension, viscometry we have used dynamic light scattering (DLS) for understanding the change in hydrodynamic size. The composition of mixed micelles, activity coefficient & interaction parameters were evaluated using Rubingh's theory .

The stability factors for micelles were also derived using Maeda's approach. Steric factor due to difference in head group of nonionic surfactant has been taken in account. Synergism in mixed micelles has been elaborated by DLS and viscosity data, which show typical trend in viscosity and linear trend for the hydrodynamic sizes. The effect of alkyl chain & counter ion on cationic surfactant and hydrophilic polyoxyethylene chain of nonionic surfactant has been discussed.

Poster FR-7

STABILITY OF AN INTERFACIAL MENISCUS FOR FILLING NANOCHANNELS

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The stability of a liquid filament between two surfaces is utilized to fill nanochannels with no residue on the rest of the top surface. The stability condition is that the average contact angle of the liquid with the surfaces be less than 45° . This condition means that a liquid that wets a surface can be used, which contrasts earlier results where liquids that readily dewet a surface are required for the filling. Experimental results are presented for filling nanochannels selectively with sol-gel solutions.

This study determines the condition under which such an interfacial meniscus becomes stable. When a readily wetting liquid is spin coated on a substrate with patterned nanochannels, a continuous liquid film forms over the ridges and grooves of the channels. If the ridges are contoured and a flat substrate is brought into contact with the liquid film over the ridges, a meniscus would form between the flat substrate and the contoured ridges. The most stable state of this interfacial meniscus would theoretically determine the condition for filling the channels with no remaining residue. Successful filling should occur for $\theta \leq \pi/4$ where $\theta = (\theta_1 + \theta_2)/2$. Here θ_1 is the contact angle the liquid makes with the flat plate and θ_2 the contact angle with the substrate.

The filling technique would pave the way to utilizing sol-gel solutions for device fabrication and for fabricating nanofluidic structures where the mechanical integrity of the structures at nanometer scale is critical and where the hydrophilicity is highly desirable for biomaterials.

Poster FR-8

ON THE DROP-SIZE DEPENDENCE OF CONTACT ANGLES

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The contact angle of a liquid droplet on a solid surface is typically characterised on the basis of macroscopic measurements. However, in many applications (flotation, nucleation, microfluidics...) the interest is in droplets of microscopic or submicroscopic dimensions. The potential dependence of contact angle on drop-size is therefore an important issue, and has received significant interest in recent years, largely due to reports of unexpectedly large values of line tension ($|\tau| \sim 10^{-6}$ J/m). Such large values of line tension would lead to a dramatic difference in contact angles between macroscopic and microscopic droplets, but are inconsistent with both theoretical predictions ($|\tau| \sim 10^{-12} - 10^{-10}$ J/m) and the results of scanning force microscopy experiments.

Here I show, through elementary theoretical considerations and illustrative experiments, that these anomalous line tension values can be attributed to deficiencies in the interpretation of the measurements on which they are based. In particular, I show that one can typically expect to observe a dependence of contact angle on drop-size for reasons which have nothing to do with line tension, and which do not result in trends which can be extrapolated from macroscopic to microscopic dimensions.

Poster FR-9

**DENSE AND SQUARE LATTICE-FREE COLLOID CRYSTALS OF
HIGHLY-CHARGED MONODISPERSE LATEX PARTICLES ON 3-
AMINOPROPYL TRIMETHOXYSILANE-MODIFIED GLASS
SUBSTRATE**

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2- and 3-dimensional colloid arrays are fabricated using highly-charged monodisperse poly (styrene/sodium *p*-styrene sulfonate) particles and 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrate at 20°C. The 2- and 3-dimensional arrays on the APTMS-modified glass substrate show denser packing patterns with no crevices, as compared with those of cleaned bare glass substrates. This dense packing pattern is explained by the nature of APTMS-coated surface leading to 'free-slipping' of incoming particles and stronger capillary force due to the hydrated and hairy surface of the particles at the water meniscus, and which leads to substantial particle deformation and hexagonal close packing. These arrays of deformed particles in the first layer then act as a template for further growth through multilayer deposition following the same packing pattern.

A NOVEL METHOD FOR HIGHLY MONODISPERSE MICRON-SIZED SILICA PARTICLES IN ROOM TEMPERATURE

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The advances of silica particles having monodisperse shape have received a lot of attention in colloidal science. Recently, the silica colloids utilize for studying such as stabilizer, chromatography, catalysis, and rheology. Especially, micron-sized monodisperse silica particles were used in many research and industrial application. However, it is difficult to satisfy both monodisperse and micron-size diameter in preparation of silica particles. Therefore, it has been widely investigated to find the more appropriate system. Also, surface modification is an important part of silica colloids and these products support to prepare hybrid materials.

In our experiments, we describe the simple and easy method that is able to prepare the monodisperse silica particles with micron-size range and functionalized surface. We use 3-mercaptopropyl trimethoxysilane (MPTMS) as a reagent and particle sizes are 1.2 μm , 2.5 μm , and 3.7 μm . There are some keys in our method. First, size of particle can be controlled by the amount of reagent. Second, we do not need any other assistants to make silica colloids. Third, for fabricating the particles, we used one-step method using ammonia catalyst for the hydrolysis and condensation in room temperature.

All samples were characterised with SEM and TEM images to confirm the morphology of the particle. We can get the properties of the particle using thermogravimetric analyser (TGA) and energy dispersive X-ray (EDX) data.

USING CAPILLARY ELECTROPHORESIS TO RAPIDLY MEASURE THE SIZE OF Au/Ag CORE/SHELL NANOPARTICLES

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NPs are currently attracting a great deal of attention in a wide variety of scientific fields [1]. The design, synthesis, and characterization of nanostructures have become very important aspects of the emerging field of the nanomaterials because the manipulation of structures has a direct effect in their macroscopic properties. In fact, the physical and chemical properties of NPs are directly related to their chemical compositions, sizes, and surface structural characteristics [2]. Recently, the surface-enhanced Raman scattering (SERS) offers a chance to increase the Raman intensities of molecules adsorbed onto rough metal NP surfaces by ca. 6 to 14 orders of magnitude, allowing the detection of the signal of a single molecule [3]. Interestingly, Au/Ag core/shell NPs are very much more SERS-active than either of their individual monometallic NPs [4]. For this reason, the fabrication of Au/Ag core/shell NPs is a research field that is currently attracting a great deal of interest, as is the study of how their SERS phenomena relate to their sizes. Therefore, manipulation of crystal growth, rapid measurement of particle sizes, and characterization of the stability of Au/Ag core/shell NPs are all critical issues if Au/Ag core/shell NPs are to be employed in SERS applications.

This work describes how capillary electrophoresis (CE) can be employed to investigate the size of Au/Ag core/shell NPs. We obtained a linear relationship ($R^2 > 0.99$) between the electrophoretic mobilities and sizes of Au/Ag core/shell NPs whose diameters fell in the range from 21.4 to 60.1 nm; the relative standard deviations of these electrophoretic mobilities were all below 1.1%. We employed these separation conditions to investigate the size of such Au/Ag core/shell NPs samples. The good correlations that existed between the results obtained using CE with those provided by scanning electron microscopy (SEM) confirmed that the CE method is a valid one for characterizing the size of Au/Ag core/shell NPs. In addition to monitoring the size of Au/Ag core/shell NPs, CE can also be employed to simultaneously characterize the size-dependent optical properties of Au/Ag core/shell NPs through spectral measurement of their migration peaks using on-line photodiode array detection (DAD) system. Our results suggest that CE analyses will be useful for accelerating the rates of fabrication and characterization of future nanomaterials.

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PREPARATION OF SODIUM ALGINATE HYDROGEL MICROSPHERES BY ELECTROSPINNING

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Alginate is a natural biopolymer extracted from brown algae. It is composed of linear chains of the α -L-guluronic acid (G) and the β -D-mannuronic acid. Alginates form hydrogels in the presence of divalent cations like Ca^{2+} .¹ Nowadays, the use of alginate hydrogels in biotechnology and pharmaceutical industry is widespread due to the unique properties such as high biocompatibility and biodegradability.

In this study, alginate hydrogel beads were prepared by using electrospinning method at diverse process parameters such as polymer concentration, applied voltage, tip to collector distance, and divalent cations. Sodium alginate was dissolved in water 70 \square for 1 h and maintained for 30 min to ensure homogenization. Concentration of alginate solution was varied form 1 to 3 g/dl.

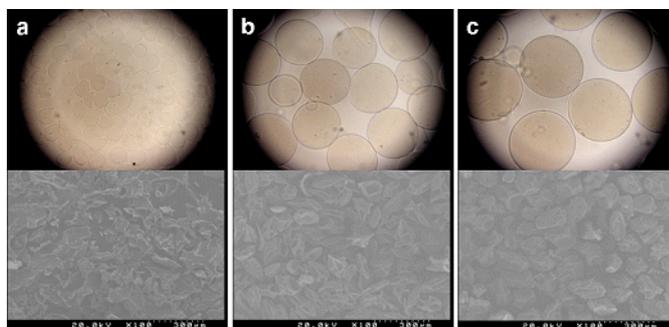


Figure 1

Figure 1 is a series of photographs presenting the morphology of alginate beads prepared at various polymer concentrations. All other parameters were kept constant at applied voltage of 15 kV, TCD of 15 cm, and 0.1 M CaCl_2 cross-linking solution. In these experiments, the size of alginate bead collected into cross-linking solution was increased as the polymer concentration was increased. However, in scanning electron microscopy image, structure of 1 g/dl alginate bead was destroyed owing to dilute CaCl_2 solution or low polymer concentration.

Acknowledgements

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PREPARATION OF HIGH MOLECULAR WEIGHT POLY(VINYL PIVALATE) PARTICLES USING EMULSION POLYMERIZATION OF VINYL PIVALATE

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To prepare high molecular weight (HMW) poly(vinyl pivalate) (PVPi) with high yield and high linearity which is a promising precursor for syndiotactic poly(vinyl alcohol) (PVA), vinyl pivalate (VPi) was emulsion polymerized using 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) as an initiator and sodium dodecyl sulfate (SDS) as an emulsifier. The effect of the polymerization conditions on the conversion, molecular weight, and degree of branching was investigated.

PVA with maximum number-average degree of polymerization (P_n) of 6,200 could be prepared by complete saponification of PVPi with P_n of 13,300 - 16,700 obtained at polymerization temperature of 50 °C using SDS and AAPH concentration of 2.0×10^{-3} mol/liter of water and 1.0×10^{-3} mol/liter of water, respectively, and the maximum conversion was about 90%.

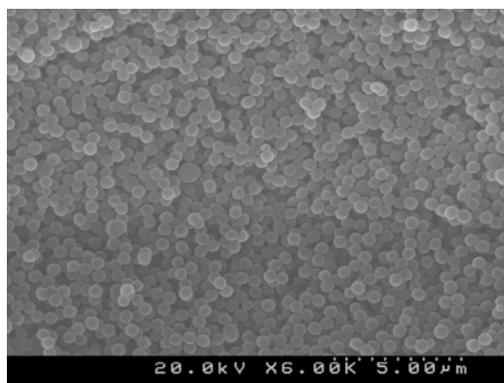


Figure 1

PVPi micro- and nanospheres was obtained by emulsion polymerization of VPi using AAPH. Figure 1 shows the SEM photograph of PVPi microspheres. Despite of original PVPi specimen directly prepared from emulsion polymerization of VPi without separation procedures like sieving, it is shown that uniform PVPi spheres with diameter of 400-500 nm could be obtained.

Acknowledgements

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE).

SURFACTANT SELF-ASSEMBLY IN ROOM-TEMPERATURE IONIC LIQUIDS: SOLVATION AND IONOPHOBIC EFFECTS

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Surfactant self-assembly has been previously shown to occur in a room-temperature ionic liquid (RTIL) that can potentially form a three-dimensional hydrogen-bond network,¹⁻³ generally regarded as a prerequisite for solvents able to support amphiphilic self-assembly.⁴ Here we report micelle and mesophase formation by non-ionic surfactants in RTILs unable to form this type of extended hydrogen-bond network.

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. Small-angle neutron and x-ray scattering and polarising optical microscopy were used to examine the self-assembly behaviour of polyoxyethylene alkyl ethers (C_nE₆, n = 12-18) in these solvents and 1-ethyl-3-methylimidazolium thiocyanate as a function of alkyl chain length, temperature and concentration.

Micelles and mesophases with well-defined structures were found to form in each surfactant-solvent system and exhibited concentration and temperature-dependent behaviour paralleling that observed in aqueous systems. Changes in micellar geometry were also observed as the ability of the RTIL to solvate the E₆ hydrophilic moiety via hydrogen bonding was varied. It is proposed that ionophobic interactions – analogous to the solvophobic interactions believed to drive aggregation in hydrogen-bonding solvents - may be present in systems where solvent structure arises from formation of an electrostatic network.

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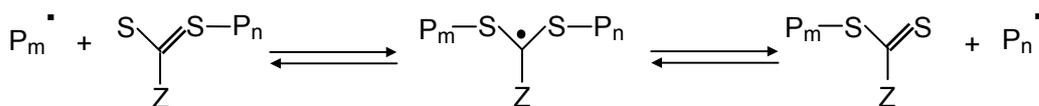
REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER POLYMERIZATION IN MICROEMULSIONS

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Reversible addition-fragmentation chain transfer (RAFT) is a robust method of controlled free radical polymerization. RAFT has successfully produced low polydispersity polymers of predetermined molecular weight in both homogeneous and heterogeneous polymerizations. However, the incorporation of RAFT in free radical polymerizations frequently results in rate retardation. Both termination and slow fragmentation of the intermediate macroRAFT radical formed during the transfer of radical activity from an active chain to a dormant chain have been proposed as the cause of rate retardation (Scheme 1). Thus far, experimental evidence for termination or slow fragmentation is inconclusive.



Scheme 1. Reversible addition of propagating and dormant polymer chains to form the intermediate macroRAFT radical.

Microemulsions provide an ideal medium for studying controlled polymerization by RAFT because biradical termination is minimized by the segregation of the propagating radicals into surfactant-stabilized polymer particles. Therefore, the significant rate retardation observed in RAFT microemulsion polymerizations necessarily arises from slow fragmentation of the macroRAFT radical. The impact of slow fragmentation of the macroRAFT radical can be quantified only after confirming that the addition of the chain transfer agent does not alter the probability of biradical termination or the partitioning of monomer between the micelle and polymer particles.

In this work, RAFT microemulsion polymerizations of butyl acrylate with the chain transfer agent methyl-2-(O-ethylxanthyl)propionate (MOEP) are investigated in terms of the Morgan model for uncontrolled microemulsion polymerization kinetics. The combined decrease in polymerization rate and shift of the rate maximum to low conversions suggests that the chain transfer agent induces nonlinear monomer partitioning. However, small angle neutron scattering experiments to monitor the microstructure of the polymerizing microemulsions confirm that the monomer partitions linearly at all MOEP concentrations investigated. The chain transfer agent has also been shown to have a negligible impact on the probability of biradical termination. Therefore, the rate retardation observed in RAFT microemulsion polymerizations arises solely from slow fragmentation of the macroRAFT radical and the lifetime of the macroRAFT radical can be quantitatively determined from the polymerization kinetics.

Poster FR-16

HETEROGENEOUS COLLOIDS: BUILDING BLOCKS FOR NOVEL CRYSTALLINE STRUCTURES?

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Charged colloidal spheres adsorbed by heteroaggregation onto an oppositely charged core particle may be evenly arranged on the surface by lateral double layer repulsion. By judicious choice of the relative satellite-core particle size ratio and the Debye length of the system the maximum number of satellite particles that may be adsorbed may be controlled. In addition, the aspect ratio of the cluster surface may be controlled by varying the relative hydrophobicity of the core and satellite particles as well as the flexibility of the satellites. The clusters formed may therefore be designed with a controlled degree of electrostatic, topographic and hydrophobic heterogeneity, yet are stable in suspension.

The crystallisation of monodisperse colloidal particles has been widely investigated, but the effect on this process of surface heterogeneities, as described here, remain largely unknown. Particular attention is paid to co-ordination number of 4, a tetrahedral arrangement of satellites around a core particle. It is hoped that by engineering the functionality of these particles in this way they will behave as so-called tetravalent 'colloidal molecules' and arrange themselves in a tetrahedral manner (similar to sp^3 bonding) when brought to an arrested state, a possible pathway for which will be discussed. This may provide a route by which diamond structured colloidal crystals may in future be fabricated, a subject that is of particular interest in the area of photonics.

APPLICATION OF WANG-LANDAU MONTE-CARLO TO POLYMER SIMULATIONS

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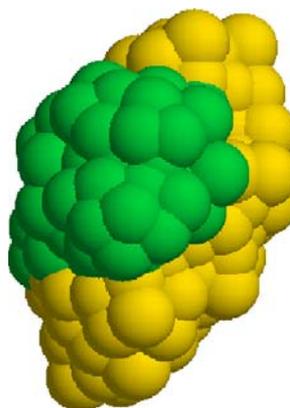
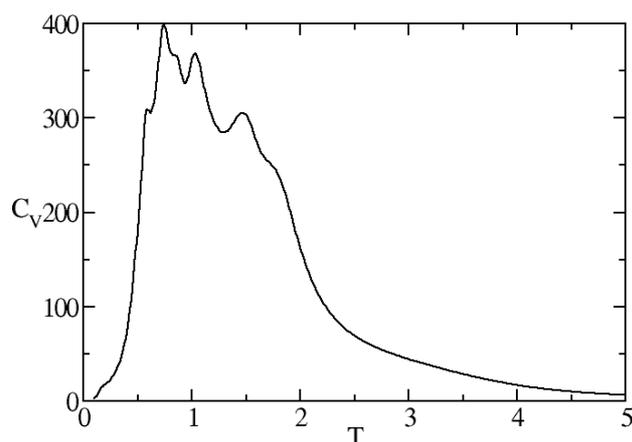
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The Wang-Landau algorithm is a novel Monte-Carlo simulation technique. It is a temperature-independent technique which directly calculates the density of states $g(E)$ over a range of energies, distinct from the traditional Metropolis Monte-Carlo algorithm which runs at one given fixed temperature. The technique enables the calculation of average quantities such as internal energy or radius of gyration over a range of temperatures, with temperature as a free parameter. The Wang-Landau technique also has certain advantages over the Metropolis algorithm when sampling in highly condensed regions of phase space.

The technique is applied to the simulation of off-lattice single chain polymers. The heat capacity calculated as a function of temperature reveals the existence of different phases within the collapsed globule, which are identified as high-density and low-density liquid-like phases.

Simulations performed on single chain multiblock copolymers identify an order-disorder transition inside the collapsed globule. A block copolymer collapses into a number of distinct clusters formed as blocks of the same type of monomer coalesce. The Wang-Landau technique enables the changing composition of the copolymer, in regards to the number of clusters, to be determined. A number of interesting and unexpected conformations are identified in this way.



THE STUDY OF POLYMER EFFECTS ON NANOSTRUCTURES SIZE IN THE MIXED CATIONIC-ANIONIC SURFACTANTS

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Aqueous mixtures of oppositely charged surfactants exhibit interesting phase behavior and properties. It is well known that vesicles form spontaneously when oppositely charged surfactants are mixed in aqueous solution [1]. Vesicles have been utilized as nanoscale vehicles for reagents including potential drug delivery systems. When use to deliver drugs, vesicles size and the size distribution are important factors in the determination of dosage, cell specificity, and rate of clearance from the body [2].

The study of surfactants and polymer interactions in aqueous solution has been a topic of intense fundamental and applied research. Surfactants-polymer systems are important in various industrial and technological fields such as cosmetics and pharmaceutical products, paints and coatings, adhesives, mineral processing and petroleum industries and many other applications [4]. Polymer has dramatic effects on the morphology of the aggregates of the equimolar mixed cationic-anionic surfactants. Furthermore, the size of the vesicles could be controlled by turning the total surfactant concentration, polymer concentration and molecular weight [3].

Previously, we investigated the transition from vesicles (microstructure) to mixed micelles (nanostructure) sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB) mixture in the very dilute region at 25°C [5]. In the present work, polymer effect was investigated on the surface activity parameters and nanostructures size in this mixture in different temperatures and concentrations. In the order of was used from surface tension and steady state fluorescence methods.

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EFFECT OF THE PECULIARITY OF WATER POOL pH OF W/O MICROEMULSION ON PARTICLE SYNTHESIS

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An interesting finding of water pool properties of W/O microemulsions was recently reported.¹ The water pool pH of AOT/n-heptane/water microemulsions was estimated using the excitation band intensity ratio of a pH-sensitive fluorescent probe pyranine in the water pool. The W/O microemulsions were prepared using aqueous solutions in the pH range of 1 - 12. It was found that the water pool pH remains almost constant in the pH range of 3 - 11, suggesting that the water pool exerts a buffer-like action.

The W/O microemulsions have been widely used to synthesize metallic or inorganic particles. It has recently been reported that the shape of the particles is controlled by addition of salts into the water pool before the reaction.² It is important to investigate relationship between properties of synthesized particles and the water pool properties. In particular, the water pool pH should be the subject of investigation because pH is one of the primary factors to control particle synthesis reactions.

In the present study, the effect of the buffer-like action on particle synthesis was investigated. The CaCO₃ particles synthesis was employed for the investigation because the crystal form and shape of the particles are dependent on solution pH. The buffer-like action for microemulsions prepared from aqueous solutions of CaCl₂ and Na₂CO₃ at pH 4 was examined. The water pool pH is estimated to be 8 by an absorbance ratio given by uv-vis absorption spectra of the pyranine. CaCO₃ particles are not synthesized by mixing the CaCl₂ and Na₂CO₃ aqueous solutions of pH 4, but the particles deposit by mixing those of pH 8. The microemulsions were mixed to examine if the buffer-like action affects the particle synthesis. As the results, the particles are not synthesized which is clarified by the finding that the microemulsion size and the absorbance ratio do not change before and after mixing the microemulsions. It thus appears that buffer-like action does not affect particle synthesis in the case of W/O microemulsions of AOT.

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Poster FR-20

COLLOIDAL SURFACE ENGINEERING: A NANOBLENDED APPROACH

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Surface modification of colloidal particles via the layer-by-layer (LbL) method has gained significant popularity since its introduction. By adsorbing alternating layers of positively and negatively charged species, a multilayer can be assembled onto a colloidal template. In most cases, the core can then be dissolved to produce hollow capsules that exhibit different physical and chemical properties. Selection of template sizes, types of adsorbing material, total number of layers deposited and post-assembly treatment conditions enables the fabrication of core-shell particles and hollow capsules that have different dimensions, functionalities and shell thicknesses. The core-shell particles and hollow capsules have subsequently found use in a wide range of applications, including catalysis, photonics, biosensing, and as encapsulation and delivery vehicles.

This study examined the assembly of multilayers that consist of three components. The three components are a weak polycation (PAH) and a blend of weak/strong polyanion (PAA/PSS). The use of a polyelectrolyte blend enables an additional degree of control over the thickness and the composition of the multilayer. In this work, we investigated the effect of blend ratio and ionic strength of the deposition solution on the relative amounts of adsorption for all three of the multilayer components. This was accomplished by measuring the fluorescence of eight-layered core-shell particles assembled with fluorescently labelled polymers. We also investigated the colloidal stability of the core-shell particles as a function of the adsorption solution composition. The feasibility of the blended system to form stable hollow capsules, in particular the role of PSS in achieving structural integrity, is highlighted. We investigated the thickness of these capsules after the assembly of eight layers, with respect to different adsorption solution compositions and ionic strengths. Capsule characterisation is performed with transmission electron microscopy (TEM) and atomic force microscopy (AFM).

The data obtained from this study allows a better understanding of the simultaneous adsorption of binary polyelectrolyte mixtures on colloids. The respective role of the blend constituents is investigated and a mechanism for their adsorption is proposed.

INTERACTION FORCES IN PLURONIC STABILIZED EMULSIONS

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Pluronics, (PEO-PPO-PEO) tri-block co-polymers, are commonly used in a wide range of applications ranging from emulsion stabilization to drug delivery due to their low toxicity and cost. Understanding the behavior of adsorbed Pluronics layers at the oil-water interface and their effect on interactions on the nanometer scale is crucial in controlling emulsion stability. However, measurements of interfacial forces at deformable interfaces are uncommon due experimental challenges. In this work, both static and hydrodynamic forces between two approaching oil droplets, stabilized with a series of Pluronics were measured by using the AFM.

The aim of this work is to develop a quantitative understanding of how polymer adsorption at the liquid-liquid interface affects inter-droplet interactions. Three different molecular weights of a Pluronic block copolymer were used as stabilizers for oil droplets in aqueous solution. The molecular weight of the polyethylene polypropylene oxide (PPO) segment, adsorbed at the oil-water interface, was kept constant as the size of the polyethylene oxide (PEO) segments, extending into the aqueous phase, were increased. Force-separation data for the different Pluronic polymers were analyzed by using an appropriate model to quantify effects of the PEO brush layer thickness on the forces and the effect of the polymer brush layer on the hydrodynamic drainage of the liquid film between the two droplets. The effect of changing solvent quality on the adsorbed polymer by changing the salt concentration in solutions will also be discussed.

PHOSPHOLIPID-STABILIZED SILICA NANOPARTICLES WITH MAGNETIC PROPERTIES AS DRUG DELIVERY SYSTEMS

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In recent years, an increasing interest has been devoted to the preparation of advanced drug delivery platforms based on various colloidal systems.

Ceramic biocompatible materials represent a growing research area in drug delivery, offering promising vehicles such as silica nanoparticles or hybrid silica-polymeric particles. These nanoparticulate systems can be used for many drugs to provide appropriate therapeutic levels and a specific biodistribution.

Using the encapsulation of magnetic nanoparticles in the colloidal vehicles, a magnetically guided or targeted drug delivery system can be obtained.

The aim of the present work is to develop a method for the preparation of a new nanopatform containing magnetic material encapsulated in silica nanoparticles with improved stability and biocompatibility.

The preparation of complex magnetic-silica nanoparticles was performed using organic modified silica precursor in W/O microemulsion as heterogeneous reaction media. The obtained hybrid nanoparticles were stabilized by using natural phospholipid derivatives in a procedure devoted to ensure the formation of biomimetic lipid bilayer on the surface of the silica particles.

TEM, ESEM and DLS measurements were used to characterize the size, morphology and surface potential of the nanoparticles.

The obtaining procedure allow the preparation of colloidal nanoparticles with narrow size distribution and better stability. The size of these particles is always in the range 50- 100 nm in diameter according to the lipid derivative used to stabilize the hybrid nanoparticles in water.

The stabilization with natural phospholipid derivatives is not only very effective but also improve the biocompatibility and due to the wide range of chemical composition offer the possibility for further functionalization, such as attachment of polyoxyethylenic groups or specific targeting moieties.

To evaluate the qualities of the new drug delivery systems, Methotrexate was used as a model drug and drug loading efficiency and release kinetic were studied.

Acknowledgment. This work was financially supported by the National Research and Development Agency of Romania, the Program of Excellence in Research (No. 51/2006 BIOTECH – CEEX).

THE EFFECT OF RELATIVE HUMIDITY ON THE PERFORMANCE AND SURFACE ENERGIES OF SALMETEROL XINAFOATE POWDERS FOR INHALATION

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This study investigated the effect of relative humidities (RH) on the performance of salmeterol xinafoate (SX) powders for inhalation stored over a six month period. Powders of five different compositions (drug alone, an SX-coarse lactose mixture without added fines and SX-coarse lactose mixtures containing 5%, 10% and 20% lactose fines) were kept at RH of 33%, 55% and 75%. *In vitro* aerosol deposition (fine particle fraction, FPF) was determined using a twin stage impinger and a validated HPLC method. The drug only formulation showed greater variability than the mixtures. The FPF of SX for all powders was not significantly different when stored at 33% and 55% RH over the six month study period. At 75%RH the FPF of SX-coarse lactose mixture containing 20% fine lactose significantly decreased from 11.3% to 7.7% within the first 8 weeks of storage; however, the FPF did not significantly change over the remaining period ($P=0.635$). All the other formulations remained almost unaffected for the whole study period. For the SX-coarse lactose mixture containing 20% fine lactose further investigation at 95%RH showed that the FPF declined to 4.88%, which is almost 57% reduction from the initial value within the first 8 weeks. The FPF gradually decreased over the remaining period. The study concluded that the critical factors in the decreased performance of SX powders for inhalation were storage humidity of 75% or greater and the presence of high concentrations of fine lactose.

IGC was used to determine the surface energies of initial and aged SX, coarse lactose, fine lactose and the two component mixture containing 20% fine lactose kept at 75%RH. Both dispersive surface free energies (γ^D) and specific surface free energies (ΔG_A^{SP}) due to interactions with polar probes (acetone, ethyl acetate, acetonitrile and ethanol) were determined. At infinite dilution (concentration: p/p_0 : 0.03), γ^D for initial SX, coarse lactose, micronized lactose and the mixture containing 20% fine lactose were 45.2 mJ/m², 39.8 mJ/m², 46.6 mJ/m² and 40.7 mJ/m² respectively. As only highly energetic sites of powder surfaces were involved at infinite dilution, the concentration was gradually increased from infinite to finite concentration to include less active sites and thus the energetic heterogeneity profiles of the surfaces were determined which showed significant differences between initial and aged samples.

FABRICATION OF MONOLITHIC FIBER WITH A MOLECULARLY IMPRINTED SURFACE: APPLICATION FOR THE ISOLATION OF MENTHOL FROM PHARMACEUTICAL PREPARATIONS

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Molecular imprinting is a technique for the preparation of synthetic polymers with predetermined selectivity for a desired template. Over the past ten years considerable progress has been made on molecularly imprinted polymers (MIP). These polymers are synthesis in the presence of template molecules. After removal of template molecules, polymers are shown to be effective in the recognition properties for its template. Their inherent advantages include reusability, simplicity, low cost, high affinity and selectivity for the target molecules, physically and chemically stability over a wide range of experimental conditions.

Menthol, a monoterpene, is a major component in essential oils of different species of mint. It is widely used in food and pharmaceutical industry as flavoring agent and in traditional phytotherapy for the treatment of some diseases. Selective and sensitive analysis of menthol in pharmaceutical preparations and human fluids has become therefore very important.

In this study, a monolithic fiber with 2 cm length and 0.3 mm diameter was prepared by thermal radical co-polymerization of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) in the presence of menthol as template molecules. These monolithic polymers were used as solid-phase microextraction (SPME) fibers for the selective extraction of menthol from various pharmaceutical and biological samples prior to GC and GC/MS analysis.

Effective experimental parameters such as MAA, EDMA and menthol proportions, nature and dimension of mold, co-polymerization time and temperature were optimized. Scanning electron microscopy (SEM) and chemical studies reveal that, homogeneous surface of fiber has MIP properties. The prepared monolithic fiber was used as a SPME fiber for selective extraction of menthol from various pharmaceutical and biological samples prior to GC and GC/MS analysis. Experimental results reveal that the proposed fiber has a high extraction efficiency and selectivity for the extraction of the selected compound from the complex aqueous pharmaceutical and biological samples.

GRANULE NUCLEUS FORMATION VIA SOLID SPREADING IN PHARMACEUTICAL WET GRANULATION

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Granulation of hydrophobic powders is a growing problem in the pharmaceutical industry. The structural complexity of new drug molecules mean that is increasingly common for entire classes of drug compounds to be highly hydrophobic. This creates considerable difficulty in understanding, controlling and trouble-shooting these industrial granulation processes.

There have been many recent advances in granulation theory (Litster and Ennis, 2004), but it is assumed that wetting and spreading of the fluid through the powder particles is a prerequisite for good granulation. The possibility of a fine, hydrophobic powder spreading over the surface of the liquid during nucleation has been identified theoretically based on surface chemistry (Rowe, 1989) and as a potential nucleation mechanism (Hapgood 2000, Simons and Fairbrother, 2000). Recently, investigation confirmed that nucleation can occur by spreading of the particles around the template drop (Farber et al., 2006). This unique nucleation behaviour is called "solid spreading nucleation".

After drying, a hollow spherical shell may be formed. The hollow granule structure formed by the solid spreading mechanism is unique and suggests the possibility of using the controlled, open granule structure to manufacture "designer pharmaceutical particles" with a number of advantageous properties:

1. Controlled granule size by manipulating the spray drop "template" sizes
2. Controlled granule structure by exploiting the solid spreading mechanism.

This allows for the potential for designer pharmaceutical particles, with controlled size distribution and excellent ideal flow and handling properties.

This poster will describe initial experimental results regarding solid-spreading nucleation and progress to date on understanding the interfacial driving forces. Single fluid drops are delivered using a syringe to the surface of a loosely packed bed of a hydrophobic powder (eg salicylic acid, contact angle with water 105°). The movement of the powder and the formation kinetics of the powder shell around the template drop will be studied. Implications for pharmaceutical granulation via solid spreading will be discussed.

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SYNTHESIS AND CHARACTERISATION OF POLYETHYLENE GLYCOL METHOTREXATE POLY-L-LYSINE DENDRIMERS

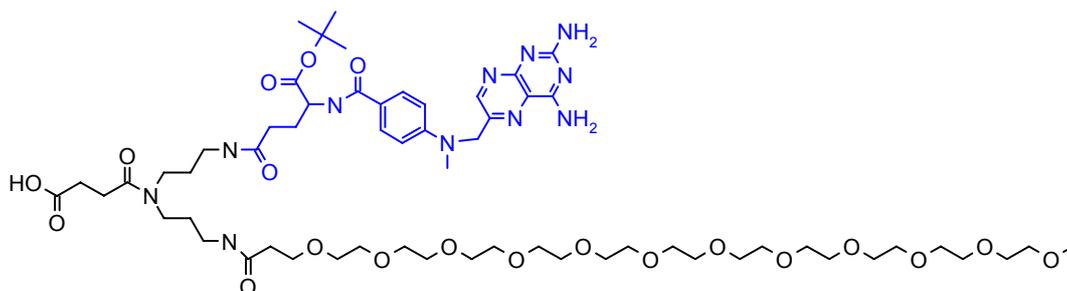
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Dendrimers have received much attention as potential carriers of cytotoxic agents due to their unique characteristics such as uniform and controlled size, monodispersity and modifiable surface group functionality (1). Unfortunately problems such as aqueous solubility, biocompatibility and availability have limited investigations to only a few classes of dendrimers. Starpharma, which already has one capped Poly-L-Lysine (PLL) dendrimer in clinical trial, is now investigating the utility of PLL dendrimers as potential scaffolds for cytotoxic drug delivery.

This poster will describe the synthesis of polyethylene glycol (PEG) methotrexate (MTX) wedges ($\text{Su(NPN)}_2(\text{MTX})(\text{PEG}_{570})$), via an orthogonally protected intermediate, along with their conjugation to radiolabeled PLL dendrimers (Generation-3,-4,-5). A range of wedges were prepared with varying PEG length (PEG_{570} , 1100, 2300) in order to tune the constructs plasma half-life. A range of analytical data (HPLC, MS) will be presented, confirming the monodispersity of the conjugates.



Su(NPN)₂(MTX)(PEG₅₇₀)

G-3	BHALys[Lys] ₄ [Su(NPN) ₂ (MTX)(PEG ₅₇₀)] ₈	11.3 kDa
G-4	BHALys[Lys] ₈ [Su(NPN) ₂ (MTX)(PEG ₅₇₀)] ₁₆	22.5 kDa
G-5	BHALys[Lys] ₁₆ [Su(NPN) ₂ (MTX)(PEG ₅₇₀)] ₃₂	45.0 kDa

(1) A. K. Patri, J.F. Kukowska-Latallo, J.R.J. Baker, Targeted drug delivery with dendrimers: Comparison of the release of covalently conjugated drug and non-covalent drug inclusion complex kinetics *Advanced Drug Delivery Reviews*, **2005**, 57, 2203-2214.

PREPARATION AND MEMBRANE FLUIDITY OF NOBLE METAL NANOPARTICLES LOADED DPPC LIPOSOMES

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Noble metal nanoparticles (silver, gold and platinum) have lately attracted considerable attentions in the applications of food, drug and cosmetics. The most effective form of noble metal nanoparticles could permeate into the cell is reported as colloidal states, not ionic fine particles. With respect to the increased interests, it is under the necessity of the research about noble metal colloids with cell membrane-like model. Silver nanoparticles have been reported as anti-microbial property and applied to the products such as soap and toothpaste. Gold nanoparticles are used as biomedical agents, natural preservative and bactericide. And platinum nanoparticles are admitted to anticancer agents, food supplements in gums or beverage.

In this study, silver, gold and platinum nanoparticles were dispersed in toluene or water as colloidal solution were respectively loaded in the dipalmitoylphosphatidylcholine (DPPC) liposome by simple preparation. The morphologies of noble metal colloids loaded liposomes investigated as spherical doughnut-like shapes by OM and HVEM. Numbers of silver, gold and platinum nanoparticles were investigated as ring-like view photograph by EDS mapping images. With the additional elemental indexing of spectrum, it is further supported that the peaks of silver, gold and platinum nanoparticles were relatively highly detected in the each liposome. The membrane fluidities the silver, gold and platinum colloids loaded liposome were changed to increased or to decreased than DPPC (noble metal nanoparticles non loaded) liposome by fluorescent anisotropy measurement. It was controlled by the types of the each noble metal nanoparticles, the dispersed medium, and the contents of each noble metal colloids.

MAGNETIC POLYMER NANOPARTICLES FOR MRI CONTRAST ENHANCEMENT

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Composite particles containing magnetic material, with wide size range and various morphologies (microspheres, nanoparticles, ferrofluids), represent the research aim for many applications, including biomedical field. Many potential applications, both for diagnostics and therapy, are made available in medicine as a result of the special physical properties of magnetic nanoparticles encapsulated in various colloidal systems.

Due to their toxicity in living systems, the particles with magnetic properties must be covered with a protective shell. This shell could be made by biocompatible polymers coupled with endstanding functional groups, allowing covalent coupling to many markers and/or therapeutic drugs.

In this work we present the preparation and characterization of nanocomposites with magnetic properties as MRI enhancement agent. The complex colloidal system was obtained in three steps, by encapsulating the previous magnetic nanoparticles in polymeric shell and further functionalization with specific targeting ligand. First step consisted in synthesis of Fe₃O₄ magnetic particles, using coprecipitation method of FeCl₂ and FeCl₃. In the second step we studied the covering procedure of magnetic nanoparticles with different types of biocompatible polymers and copolymers (hyaluronic acid, vinyl acetate - maleic anhydride copolymer, chitosan and polyallyl amine) using layer-by-layer technique. In step three, using polymer analogue reactions, we studied the possibility to attach some types of markers such as folic acid. The heterogeneous structure of the particles prepared in this work can confer both magnetic-field responsiveness and potential applicability as a drug carrier.

The size and morphology of composite nanoparticles were investigated by electron microscopy and dynamic light scattering. Obtaining procedure was extensively investigated in order to control the core-shell size ratio. The goal is to obtain new composite material with tunable properties, which displays an intermediate behavior between magnetite and polymeric nanoparticles.

The quality of the polymer coating was analyzed by comparing the infrared absorption spectra, and the electrical, thermodynamic and chemical surface properties of the composite particles, to those of the pure magnetite and polymer colloids.

In conclusion, a reproducible procedure for coating magnetic colloidal nanoparticles with a shell of biodegradable polymer is performed in order to obtain a better MRI contrast agent.

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PROPERTIES OF NOVEL NON-VIRAL DNA TRANSFECTION AGENTS

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Our present studies are part of a program aimed at designing novel non-viral transfection agents (TAs) with significantly increased efficiency. Other studies have shown that transfection can be achieved with cationic surfactants that dimerise after an initial ion-ion interaction with DNA. We have designed a novel series of cationic TAs that include one thiol group to further explore this approach.

The purposes of the present work are: (i) to examine the rates of loss of the monomeric TA (mainly through dimerisation) over time scales that are relevant to transfection; (ii) to measure their CMC ranges; (iii) to examine the nature of the interactions between the DNA and TAs; and (iv) to determine the size of the particles formed by the interaction of the DNA and TAs.

Very little is known of the exact mechanisms by which the TA/DNA complexes form and how different conditions affect their properties, yet it has been demonstrated that even small changes in some protocols can produce greatly different outcomes. Most of the research to date has largely focussed on a “black box” approach, looking only at the transfection efficiency to determine the success or failure of various chemicals as TAs.

It is our aim to elucidate some of the poorly known properties of these TAs in order to gain a better understanding of the mechanisms underlying the complex formation processes that occur. Determining how to make reproducible, homogeneous and efficacious systems is important for the development of future TAs that would be viable as pharmaceutical products.

Using various techniques we have already been able to determine the CMC of the TAs in volumes as low as 50 μ L as well as measuring the oxidation profiles of the TAs using HPLC in the absence and presence of DNA. A beginning towards understanding the types of interactions that occur upon the formation of the DNA/TA particles along with the extent to which these interactions occur has also been made.

Transfection studies using the same TAs as this work have already shown in vitro transfection activity approaching that of Lipofectamine[®], the present gold standard.

MOLECULAR DYNAMICS SIMULATIONS OF LIPID FORMULATIONS WITH DRUG MOLECULES

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Many drugs are lipophilic and exhibit low aqueous solubility, reducing oral bioavailability. This can be vastly improved by incorporation into a lipid formulation, with some commercial products currently using this technique. Development procedures for lipid formulations and a given drug is currently based on a try and see approach, not an understanding of the underlying phenomena. We are investigating the use of molecular dynamics simulations to assist the development of new lipid based drug formulations.

In this study, we report on molecular dynamics simulations of the spontaneous structuring behaviour of the mono- (MGL), di- (DGL) and tri- (TGL) lauroyl glyceride from an initial random distribution, plus the interaction of drug molecules with these systems. GROMACS was the software package used to perform the MD simulations, utilising an united atom forcefield, bond constraints and atomic mass redistribution to achieve a 5 femtosecond time step. The simulation times for the MDS performed are 50 nanoseconds.

The organisation and dynamics of the resulting structures for various compositions are analysed, including the influence of increasing water concentration. The water composition for a 1:1:1 MGL:DGL:TGL weight ratio system was varied from 0 to 20 % w/w. The formulations formed reverse micellar structures (water pools bounded by hydrophilic glyceride headgroups and surrounded by alkane chain regions). Reverse micelles form even in the absence of water. Increasing the water content causes the spherical water pools to swell and changes the molecular distributions. These simulations indicate that these types of lipid formulations exhibit micro structuring. The location of model drug molecules within these various formulations was also observed, providing insight into how dilution of the lipid formulation with an aqueous phase changes the behaviour of the drugs.

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Bold face indicates a presenting author.

Italics indicates a poster presentation.

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