

19TH
AUSTRALIAN COLLOID AND SURFACE CHEMISTRY
STUDENT CONFERENCE

MURRAMARANG
SEPTEMBER 22-27, 1996

HOSTED BY
THE AUSTRALIAN NATIONAL UNIVERSITY

19TH
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STUDENT CONFERENCE
PREFACE

The conference has expanded greatly from what it was in 1967, as has the colloid community in Australia. This has implied a need to go to places with a larger accommodation capacity. There has been some concern that the ambience that has made this conference so different from others be maintained.

A few small changes have been made to assist with keeping this atmosphere. Poster sessions have been very successful at past conferences and can provide new and more senior students with a chance to present their work and gather useful comments. The ratio of posters to talks at this conference has been increased. This hopefully will allow each student to present their work without burdening the audience with an unmanageable number of talks. It is anticipated that students will attend 2-3 student conferences within the duration of their studies. Thus each student can hope to present a talk to the community at least once. To assist those students speaking, appendices have been included in this program to briefly introduce the major techniques or methods used by students. It is hoped that this will free the students to talk in more detail about their work. These appendices are not comprehensive and if successful will be augmented for future conferences.

One other change at this conference is the introduction of prizes for the best talk and the best poster. In each case the prize will be an engraved pewter mug, presented at the conference dinner.

The conference venue was chosen in keeping with the relaxed venues of past conferences. Thanks goes to the owners of the Murramarang Resort and to Sue Brearley for helping with the necessary organisation.

Special thanks, as always go to Diana Wallace for her efforts.

David Williams, Tim Senden and Edie Sevick

Past Australian Colloid and Surface Chemistry Student Conferences.

| LOCATION | HOST | YEAR |
|---------------------|----------------|------|
| Sydney | U of Sydney | 1967 |
| Melbourne | U of Melbourne | 1969 |
| Sydney | U of Sydney | 1972 |
| Melbourne/Blackwood | U of Melbourne | 1973 |
| Pretty Beach | U of Sydney | 1974 |
| ANU | ANU | 1976 |
| Blackwood | U of Melbourne | 1977 |
| Yarrawood | U of Sydney | 1978 |
| Kioloa | ANU | 1980 |
| Mt Eliza | U of Melbourne | 1982 |
| Yarrawood | U of Sydney | 1983 |
| Roseworthy | SAIT | 1985 |
| Kioloa | ANU | 1987 |
| Albury | U of Melbourne | 1988 |
| Camden | U of Sydney | 1990 |
| Roseworthy | U of SA | 1991 |
| Deakin U | U of Melbourne | 1993 |
| Fairy Meadow | U of Sydney | 1995 |
| Murramarang | ANU | 1996 |

CONFERENCE TIMETABLE

MONDAY

10:30 - 11:00 Morning Tea
12:15.....Lunch
14:00.....Talks Commence
15:00.....Afternoon Tea
15:30.....Talks
18:00.....Dinner

TUESDAY

9:30-10:30..Talks
10:30-11:00.Morning Tea
11:00-12:00.Talks
12:15.....Lunch
14:00-15:00..Talks
15:00-15:30..Afternoon Tea
15:30-16:30..Talks
18:00.....Dinner
20:00-21:00..Posters

WEDNESDAY

9:30-10:30..Talks
10:30-11:00.Morning Tea
11:00-12:00.Talks
12:15.....Lunch
18:00.....Dinner
20:00-21:00..Posters

THURSDAY

9:30-10:30..Talks
10:30-11:00.Morning Tea
11:00-12:00.Talks
12:15.....Lunch
14:00-15:00..Talks
15:00-15:30..Afternoon Tea
15:30-16:30..Talks
18:00.....Farewell Dinner

FRIDAY

9:30-10:30..Talks
10:00Check out from rooms.
10:30-11:00.Morning Tea
11:00-12:00.Talks
Conference Closes

19TH AUSTRALIAN COLLOID AND SURFACE CHEMISTRY STUDENT CONFERENCE

PROGRAM

talk duration. 20 mins per student (including questions)

Monday 23rd

Afternoon Session

Electroacoustic Study of the Renneting of Casein Micelles
THERESA WADE, School of Chemistry, The University of Sydney

Supercritical extraction of hydrophilic molecules
BRENDA HUTTON, Department of Chemical Engineering, The University of Melbourne

Structure-Property Relationships of Glucose-Based Surfactants
BEN BOYD, CSIRO Division of Chemicals and Polymers &
Department of Chemistry, The University of Melbourne

Structure of Poly(propylene oxide)/Cationic Worm-like Micelle Mixed Solutions
MARTA A. CASSIDY, School of Chemistry, The University of Sydney

Characterization of TAC8: A surfactant with cation complexing potential.
LISE ARLETH Institute of Mathematics and Physics, University of Roskilde, Denmark.

A New Technique to Monitor Surface Charge
P.A. CONNOR, Department of Chemistry, The University of Otago.

Imaging surfactant self-assembly at the solid-liquid interface using atomic force microscopy
HEATHER N. PATRICK, Department of Chemistry, The University of Sydney.

Tuesday 24th

Morning Session

Adhesive Behaviour of Thin Viscoelastic Polymer Films
BENJAMIN FRANCIS, School of Applied Physics and Ian Wark Research Institute, The
University of South Australia

Surface Force Measurements in Structured Surfactant Solutions
DAVID ANTELM, Department of Applied Mathematics, Research School of Physical
Sciences & Engineering, The Australian National University

Deformation of a Fluid Drop under Surface and Hydrodynamic Forces
JASON CONNOR, School of Applied Physics and Ian Wark Research Institute, The
University of South Australia

Adhesion between colloidal silica as seen with direct force measurement
DAVID ATKINS, Department of Applied Mathematics, Research School of Physical Sciences & Engineering, The Australian National University

Particle-bubble Interaction in Single Bubble Flotation
ZONGFU DAI, Ian Wark Research Institute, The University of South Australia

The Ultrasonic Dissolution of Aqueous Colloids
JOE SOSTARIC, School of Chemistry, University of Melbourne

Afternoon Session

A Sims And XPS Investigation Of Water Plasma Modified Aluminium Oxide Surfaces
BARRY J. WOOD, Department of Chemistry, The University of Queensland

Comparison of Bauxite Residue Suspensions
NICK PASHIAS, Department of Chemical Engineering, The University of Melbourne

Growth of Crystalline Zinc Sulfide Thin Films by Single Source Chemical Vapour Deposition
NGUYEN H. TRAN, School of Chemistry, The University of New South

Mechanism of Scale Formation in Bayer Liquors
MARK BARNES, Ian Wark Research Institute, The University of South Australia

In Situ FTIR Investigation of Adsorption at the Metal Oxide / Aqueous Interfaces
KEVIN D. DOBSON, Department of Chemistry, The University of Otago

A Comparison of Bonds Formed Between Epoxy Adhesive and Aluminium Pre-Treated with Phosphonate and Silane Compounds
ANDREW RIDER, School of Chemistry, The University of New South Wales

Wednesday 25th

Morning Session

The ACME Guide to Cheating with an AFM
IAN LARSON, School of Chemistry, The University of Melbourne

Particle-Particle Interactions Using Atomic Force Microscopy and Rheology Measurements
PETER HARBOUR, CSIRO Division of Chemicals and Polymers

Force measurements between oxide and sulphide surfaces using colloid probe microscopy
GARY TOIKKA, Ian Wark Research Institute, The University of South Australia

The Electrokinetics of Latex Particles Covered with Temperature Sensitive Hydrogel Layers
ADRIAN RUSSELL, School of Chemistry, The University of Melbourne,

The Effect of Rheology on Coalescence Phenomena in Emulsion Systems
DIANNA GOODALL, School of Chemistry, The University of Melbourne

A Spectroscopic Study of Polymers in Shear Flow Fields
SAM GASON, Department of Chemical Engineering, The University of Melbourne

Thursday 26th

Morning Session

The Relationship between Surface Chemistry and Rheology for both Symmetric and Asymmetric Colloidal Suspensions
STEPHEN B JOHNSON, School of Chemistry, The University of Melbourne

Rheology of Aerosol-OT Microemulsions
NASEEM HAWASHIN, School of Chemistry, The University of Sydney

Surfactant Enhanced Black Coal Dewatering
JAMES TUDOR, School of Chemical Sciences, Swinburne University of Technology

Surface Studies of Organics in Coal
CLEMENT CHAO, School of Chemistry, The University of New South Wales

Adsorption of Organic Molecules on to Mineral Surfaces
ROD HARRIS, School of Science and Engineering, La Trobe University

Surface Adsorption of Detergent on the Wool Fibre Surface
NARELLE BRACK, School of Chemistry, The University of New South

Afternoon Session

Effect of Polydispersity on the Crystallisation of Hard Sphere Colloids
STUART HENDERSON, Applied Physics, Royal Melbourne Institute of Technology

Single Particle Motions in Concentrated Colloidal Suspensions
TIM MORTENSEN, Applied Physics, Royal Melbourne Institute of Technology

Evaporation Resistances of Octadecanol and Cholesterol
CATHY MCNAMEE, Department of Chemistry, The University of Queensland

Interaction of Ions and Molecules with Phospholipid Monolayers and Bilayers
RUTH YOUNG, Department of Chemistry, The University of Queensland

Structural Effects of Yielding of Suspensions in Compression
MATTHEW D GREEN, Department of Chemical Engineering, The University of Melbourne

A Study of the Dynamics of a Binary Hard Sphere Colloidal System.
STEPHEN WILLIAMS, Applied Physics, Royal Melbourne Institute of Technology

Friday 27th

Morning Session

The Role of Adsorption in the Adsorbing Colloid Flotation of Sulphate
JULIE ANGEROSA, School of Chemical Sciences, Swinburne University of Technology

Adsorption Behaviour of Cationic Polyelectrolytes and Surfactants on Silica
K.E. BREMMELL, The University Of Newcastle

Ion Flotation: The Selective Binding of Counterions at a Cationic Surfactant Film
BETTY THALODY, School of Chemistry, The University of Sydney

Understanding the Development and Characterisation of Microporosity in Coal-Based Carbons
GAMINI AMARASEKERA, School of Chemical Sciences, Swinburne University of Technology

Characterisation of Coal Functionalities Using Vapour-Phase Derivatisation XPS
D. FERGUSON, Department of Chemistry, The University of Queensland

The Dissolution of Pyrrhotite in Acid Media
JOAN E. THOMAS, Ian Wark Research Institute, The University of South Australia

POSTER SESSION A (TUESDAY EVENING)

Electroluminescence from Polycrystalline Semiconductor Electrodes
KIYONOBU TANNO, School of Chemistry, The University of Melbourne

Characterisation of Thin Ferroelectric Films
CATHERINE WHITBY, School of Chemistry, The University of New South Wales

Dynamic Mobility of Small Particles
SOPHIE GIBB, School of Chemistry, The University of Sydney

Consolidation of Flocculated Colloidal Material
JANINE L. BURNS, Department of Chemistry, The University of Newcastle

Non-Equilibrium Interaction Forces Between Adsorbed Polymer Layers
SHARON WATT, Department of Chemistry, The University of Newcastle

Interaction Forces Measured between Silica Surfaces in Solutions of Polystyrene Sulphonate and CTAB.
GEORGE MAURDEV, School of Chemistry, The University of Melbourne

Effect of hydrophobicity of substrate on surface aggregate formation
CISSIE ABRAHAM, School of Chemistry, The University of Sydney

Molecular Modelling of the Adsorption of Sulphonated Naphthalenes onto Graphite Surfaces
ANTHONY O'DEA, Ian Wark Research Institute, The University of South Australia

Electroacoustic and Dielectric studies of the coating process of TiO₂.
ALEX DJERDJEV, James Beattie
School of Chemistry, The University of Sydney, NSW 2006

Reversible Surface Wetting And Particle Adsorption
SCOTT ABBOTT, Ian Wark Research Institute, The University of South Australia

Foam Stability and pH Changes During Foam Formation
PAJAREE RAJATANAVIN, School of Chemical Sciences, The Swinburne University of Technology

A Study of the Surface Structure and Reactivity of Metal Oxides
DARREN J. SIMPSON, Ian Wark Research Institute, The University of South Australia

Surface Characterisation of Mixed Oxides
JUSTIN DANN, The Swinburne University of Technology

Spectroelectrochemistry of Colloidal Silver
THEARITH HUY UNG, School of Chemistry, The University of Melbourne

Bubble Nucleation and Growth in Solutions Supersaturated with a Gas
SOPHIE F. JONES, K.P. Galvin and G.M. Evans
Department of Chemical Engineering, University of Newcastle.

POSTER SESSION B (WEDNESDAY EVENING)

Application of TOFSIMS to in situ analysis of the surface and sub surface region of individual mineral grains in coal
BIN GONG, School of Chemistry, The University of New South Wales

Analysis of Hollow Fibre Liquid Membrane Designs for Cr(IV) Removal in Electroplating Rinse Waste
PETER J HARRINGTON and Geoff W Stevens, University of Melbourne and City West Water

ATR Spectroscopy of Metal Ion Extraction
PARISA DELJOUIE RAKHSHANDEH, Department of Chemical Engineering and School of Chemistry, The University of Melbourne

Effect of the Substrate Temperature on the Preferred Orientation of ZnO Films Grown by Single Source Chemical Vapour Deposition
LEONG MAR, School of Chemistry, The University of New South Wales

The Fragmentation Reaction of Basic Zinc Acetate on heated Si(100)
MICHAEL H. KOCH, School of Chemistry, The University of New South Wales

Characterisation Of Ultrasonically Initiated Polymerisation
MARTIN KELLY, Department of Chemistry, The University of Newcastle, Callaghan,
NSW 2308

Stability of Intralipid Emulsions
IMAN HAIDAR, School of Chemical Sciences, The Swinburne University of
Technology

Effect of pH on the Rheological Properties of Colloidal Alumina Dispersions
ZHONGWU ZHOU, Department of Chemical Engineering, The University of
Melbourne

Dynamics of Film Formation
FLEUR MARSHALL, School of Chemistry, The University of Sydney

Selective Flotation of Metal Cations: Effect of Macrocyclic Complexation
JAMIE SCHULZ, School of Chemistry, The University of Sydney

*Surface and Electrochemical Studies in the Selective Flotation of Copper and Arsenic
Minerals*
DAMIAN FULLSTON, Ian Wark Research Institute, The University of South Australia

*The effect of particle surface coatings on the adsorption of orthophosphate using
Sedimentation field-flow fractionation.*
JASON VAN BERKEL, Water Studies Centre, Monash University

Cadmium(II) Adsorption on Kaolinite, a Two Stage Process
MICHAEL ANGOVE, School of Science and Engineering, La Trobe University

Thermogravimetric and Differential Thermal Analysis (TG-DTA) of Australian Coals
TRAVIS J. FITCH, The Swinburne University of Technology

Study of the Extraction Kinetics of Nickel by LIX 84
DALLAS WARREN, Department of Chemical Engineering, The University of Melbourne

Surface Charging Mechanisms Of Solids In Contact With Nonpolar Liquids
GE WU, School of Chemical Technology and Ian Wark Research Institute, The
University of South Australia

ABSTRACTS

Electroacoustic Study of the Renneting of Casein Micelles

THERESA WADE, James Beattie
School of Chemistry, University of Sydney, NSW 2006.
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When rennet is added to milk, coagulation eventually occurs. This phenomenon is exploited in the manufacture of most cheese varieties. Rennet splits a specific bond of κ -casein; a protein that forms part of the casein micelles in milk. The splitting of this bond destabilises the casein micelles, resulting in coagulation.

The zeta potential and size of the casein micelles during the renneting process has been monitored with the technique of electroacoustics. The zeta potential was almost halved from -19 to -13 mV, as the rennet split the κ -casein bond, in agreement with other findings [1]. There was an initial substantial decrease in diameter of $\sim 0.2 \mu\text{m}$, followed by an increase in size, due to the aggregation of the casein micelles once most of the κ -casein had been cleaved. The initial significant decrease in size obtained with electroacoustics has not been observed previously [2,3].

It has been postulated that the large initial size decrease observed with electroacoustics is due to the structure of the casein micelle becoming increasingly porous as the κ -casein is cleaved. O'Brien [4], has developed a theory for the dynamic mobility of a porous particle and found that the porous particle has a much higher mobility at high frequencies than a solid particle of the same radius. The porous particles would therefore appear to be much smaller than for a solid particle of the same radius. Hence, it is possible with electroacoustics to obtain structural information about the casein micelle during the renneting reaction.

1. Dalglish, D. G. *Journal of Dairy Research* 1984, 51, 425-438.
2. Walstra, P., Bloomfield, V. A., Wei, G. J., Jenness, R. *Biochimica et Biophysica Acta* 1981, 669, 258-259.
3. Horne, D. S., Davidson, C. M. *International Dairy Journal* 1993, 3, 61-71.
4. O'Brien, R. W. *Journal of Colloid and Interface Science* 1995, 171, 495-504.

Supercritical extraction of hydrophilic molecules

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Over the past two decades, an increasing amount of research has been undertaken on the uses of supercritical extraction in relation to the food industry. The benefits of this research has included the evolvement of industrial processes such as tea/coffee decaffeination (1), and hop extraction for beer production (2).

One of the major limitations of supercritical extraction encountered throughout the years has been the non-polar nature of the solvent - supercritical carbon dioxide. This has created problems in applying the process to the extraction of hydrophilic molecules, for example, proteins, enzymes, and water-soluble pigments.

The aim of this research is to modify the existing process in such a way that extraction of hydrophilic molecules may become possible. It is intended to introduce surfactants into the supercritical phase to form reverse micellar structures. This will provide a permanent micropolar phase in which polar molecules may solubilise in.

References:

- (1) Paulaitis, M. E., Krukonis, V. J. et al. "Supercritical Fluid Extraction". *Supercritical Fluid Extraction 1* (2) 1983: no page.
- (2) Hubert, P., Vitzhum, O. "Fluid Extraction of Hops, Spices, and Tobacco with supercritical Gases". *Angew. Chem. Int. Ed. Engl* 17 1978: 710 - 15.

Structure-Property Relationships of Glucose-Based Surfactants

BEN BOYD^{1,2}, C.J. Drummond¹, D.N. Furlong¹, F. Grieser², and P. Wynn-Hatton³

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Alkyl Polyglucosides are increasingly being used as replacements for petrochemical derived surfactants in "environmentally friendly" household products. Commercial alkyl polyglucosides, prepared by the Fischer route, are complex mixtures of α - and β -anomers of mono- and oligo- glucosides. The α : β ratio is approximately 65:35 and the average degree of polymerisation (DP) of the commercial alkyl polyglucosides is of the order of 1.3 to 1.7. Alkyl mono- and di-glucosides may comprise over 90% of the mixture, and there are sequentially decreasing amounts of higher polyglucosides. Little is known about the physico-chemical properties of the individual components that comprise alkyl polyglucosides, and how to optimise combinations of these components to gain the most desirable application oriented properties.

This work seeks to establish the structure-property relationships of alkyl polyglucosides, through a systematic study of the physico-chemical properties of the individual pure components of the commercial alkyl polyglucoside mixtures. A comparison of pure alkyl α -D-glucosides, alkyl β -D-glucosides, alkyl α -D-maltosides, alkyl β -D-maltosides, and model mixtures thereof with alkyl polyglucosides of various DP prepared by the Fischer route, is in progress. These studies involve the octyl, decyl, dodecyl, tetradecyl and hexadecyl homologues. Several of the individual alkyl glucosides in this matrix have been synthesised and purified to a high degree of anomeric purity. Surface tension, interfacial tension measurements and the lyotropic liquid-crystal phase behaviour of some of these surfactants have been investigated and will be discussed in terms of the surfactants' structure.

Structure of Poly(propylene oxide)/Cationic Worm-like Micelle Mixed Solutions

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For many years it was assumed that there was little or no associative interaction between cationic surfactants and nonionic polymers in aqueous solution. However, when water is replaced with 25mM solution of tetradecyltrimethylammonium bromide (TTAB), the cloud point of a 10gL⁻¹ solution of 1000 Dalton poly(propylene oxide), PPO, is raised from 32C to 53C, providing evidence for an attractive interaction between the polymer and TTAB. Addition of salicylate, an ion which promotes the growth of TTAB micelles into cylinders and worm-like structures, reduces the cloud point to a minimum of 36C at 0.1M salicylate, suggesting a weakening of the polymer-surfactant interaction.

Previous studies have shown that the addition of PPO to a solution of TTAB+salicylate solutions causes the worm-like micelles to revert to spheres. In this paper we present rheological data demonstrating the loss of viscoelasticity associated with this transformation, and correlate this with spectroscopic probe measurements of the micellar surface potential and the zeta-potential of the micelles or micelle/polymer complexes. We have previously demonstrated that measurement of these two quantities gives a valuable description of the structure of the adsorbed counterion layer in salicylate-containing micellar systems. Charge reversal can be seen in the zeta potential when salicylate is added well above stoichiometric quantities, whereas surface potentials remain positive. Despite significant changes in rheology and hence micellar structure, the surface potentials are only slightly affected by polymer adsorption, suggesting that salicylate is not being expelled from its intercalated position between surfactant head groups by competition with adsorbing PPO.

Characterization of TAC8: A surfactant with cation complexing potential.

LISE ARLETH¹, Dorthe Posselt¹, Didier Gazeau², Chantal Larpent², Thomas Zemb², Kell Mortensen³ and Jan Skov Pedersen³

¹Institute of Mathematics and Physics, University of Roskilde, Denmark.

²Service de Chimie Moléculaire, CE Saclay, France.

³Department of Solid State Physics, Ris National Laboratory, Denmark.

TAC8 is a new surfactant molecule. Two octyl-chains form the hydrophobic part of the molecule. The hydrophilic part is made of two glucose groups and a cyclam ring. This gives the molecule a potential for complexing metal ions or molecules. Surface tension measurements show that both pure TAC8 and of TAC8 with equimolar complexed CuF₂ form micelles in aqueous solutions. From a combination of small-angle neutron and X-ray scattering the shape and dimensions of the micelles are determined. Analysis of the scattering data show that both the pure TAC8 and the TAC8 with complexed CuF₂ aggregate into short cylindrical micelles with aggregation numbers of approximately 20.

A New Technique to Monitor Surface Charge

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Knowledge of surface charge is vitally important in any understanding of a material's surface properties and how it interacts with its environment. This new method gives the surface charge of solid layers and, at the same time, can also give information about the nature of the interactions between the surface and the species near it.

The surface charge is detected by using Attenuated Total Reflectance Infrared (ATR IR) spectroscopy to follow the enhanced concentration of IR active ions when they are attracted to the charged surface. By flowing solutions, containing the IR active ions at various pH, over the surface to be studied, the varying IR peak heights give the pH dependence of the surface charge.

If an accurate surface charge measurement is wanted, from any method, only indifferent ions can be used. This is ensured here, as chemically adsorbed species are easily detected by the change in their IR fingerprints from that of solution species¹. Also the chemically adsorbed species are highly concentrated at the surface giving very large IR signals, detectable to below 10^{-6} mol dm⁻³ in some systems. This allows the surface charge dependence of chemical adsorption to be easily followed by including small amounts of the adsorbing species in the flow solutions.

So far this method has been successfully applied to various metal oxide sol-gel layers, and some proteins. This new method complements traditional surface charge measurements, and is particularly useful for immobilised materials and thin films.

Reference

1 P A Connor, K D Dobson, & A J McQuillan; Langmuir 1995, 11, 4193

Imaging surfactant self-assembly at the solid-liquid interface using atomic force microscopy

HEATHER N. PATRICK
Department of Chemistry, The University of Sydney

The influence of a solid surface on the bulk solution aggregation behaviour of surfactants is not understood. Atomic force microscopy was used to image surfactant self-assembly patterns at the solid-liquid interface. The electrical double-layer force was used to image ionic surfactants. Non-ionic surfactants were imaged using a steric force. The effect on surface aggregation was studied for a series of poly(ethylene oxide) dodecyl ethers on various substrates.

Adhesive Behaviour of Thin Viscoelastic Polymer Films

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While the application of polymers has flourished within the adhesive industry over the last few decades, including extensive mechanical and fracture characterisation, there still exists only a minimum of fundamental knowledge concerning viscoelastic polymers of the order of nanometre to micron thickness. Considerable information on the behaviour of polymer melts in thin films has been obtained using the Surface Force Apparatus (SFA) in conjunction with standard hydrodynamic theory, yet little emphasis has been placed on the adhesive nature of the polymeric films. The macroscopic characterisation of thin adhesive layers has likewise been limited to quite simple tests, which often produce misleading results tending to obscure the mechanisms behind adhesive processes. The Double Cantilever Beam (DCB) technique, traditionally used in elastic fracture experiments, will be modified to examine the role of bulk and interfacial properties of polymers. Both of these techniques will be used concurrently on simple, model viscous and viscoelastic systems, such as polydimethylsiloxane (PDMS), to examine more fundamental aspects of adhesion.

Surface Force Measurements in Structured Surfactant Solutions

DAVID ANTELM

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The behaviour of an L_3 (sponge) phase in a confined geometry was studied using the Surface Force Apparatus (SFA). The force-distance profiles show two distinct force regimes due to a phase transition from the sponge phase to the lamellar phase at a critical surface separation. The characteristic force-distance profile due to the lamellar phase could be analysed to extract the characteristic spacing, modulus of compressibility, and the nature of the defects within the structure. Interestingly, the defect observed in the induced lamellar phase was an edge dislocation of Burgers vector 2. This is topologically equivalent to a handle joining two membranes, which is the basis of the sponge phase. Separate SFA measurements in the pure lamellar phase mirrored the results of the induced lamellar phase.

Deformation of a Fluid Drop under Surface and Hydrodynamic Forces

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An understanding of the forces acting across thin liquid films is important for both fundamental and commercial reasons. Bubble/particle attachment; colloid stability; wetting and spreading dynamics; foam stability; and lubrication all have surface force components which contribute to their behaviour.

Forces acting between solid surfaces have been studied extensively using the Surface Force Apparatus and Atomic Force Microscope. There are however fewer studies investigating the forces acting across surfaces where a least one of the surfaces is a fluid and therefore highly deformable. In this case deformation occurring due to the presence of surface and hydrodynamic forces will influence the interaction between the surfaces appreciably.

Thin aqueous films bounded by the surfaces of mercury (a fluid) and mica (a solid) are being investigated using a new experimental technique. This novel technique combines features of the Israelachvili Surface Force Apparatus and the Dropping Mercury Electrode, to enable an experimenter to control and measure the forces (dynamic and equilibrium) acting across the liquid. Fringes of Equal Chromatic Order (FECO) interferometry is used to measure the film thickness and provide shape information about the deformable fluid/aqueous interface.

By combining the above experimental technique and a theoretical model of the system we are able to investigate the influence deformation has on surface and hydrodynamic forces. An outline of the experimental technique and a combined experimental and theoretical description of the drops' behaviour, based on initial experimental results, will be presented.

Adhesion between colloidal silica as seen with direct force measurement

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Silica sols¹ exhibit anomalous colloidal behaviour¹⁻³. In regimes where the aqueous dispersions exhibit stability, despite an inadequately stabilizing electrical double layer interaction, an additional short-range repulsion has been suggested¹⁻⁵ and signaled from force balance studies⁶⁻¹³. However, in none of the previous force measurements has any attraction or adhesion been observed that might account for the known flocculation of silica dispersions. This discrepancy arises from surface-altering treatments of the silica used and an exceedingly slow rate of rehydroxylation to restore the native hydrated surface state^{1,14}. To overcome this difficulty, the force between layers of nanometric colloidal silica particles adsorbed from solution was measured using a surface force apparatus.¹⁵ Coating substrates with nanometric particles gives a surface smooth at the nanometre scale only, but which is fully representative of a colloidal silica-water interface. Force measurements and colloidal stability can thus be compared leading to direct evidence of a chemical adhesion between silica particles.

1. Iler, R.K., *The Chemistry of Silica*. (John Wiley & Sons, New York, 1979).
2. Allen, L. H. & Matijevic, E. *J. Colloid Interface Sci.* **31**, 287-296 (1969).
3. Allen, L. H. & Matijevic, E. *J. Colloid Interface Sci.* **33**, 420-429 (1970).
4. Tadros, T.F. & Lyklema, J. *J. Electroanal. Chem.* **17**, 267-(1968).
5. *Faraday Discuss. Chem. Soc.* **65**, 43-57 (1978).
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Particle-bubble Interaction in Single Bubble Flotation

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Particle collection by captive gas bubbles is a fundamental process in mineral flotation. The efficiency of the process, the collection efficiency, is a product of its subprocess efficiencies, i.e., the product of bubble-particle collision efficiency, attachment efficiency and stability efficiency of the bubble-particle aggregate. In this study, a single bubble flotation setup was established and a model system, which consists of nitrogen gas bubbles and broken quartz particles or smooth glass spheres which have been methylated to different but known degrees of hydrophobicity, was used to experimentally investigate the influences on collection efficiency of particle surface hydrophobicity, particle size, bubble size, electrolyte concentration and pH value. It was found that collection efficiency increases with increasing particle hydrophobicity and electrolyte concentration but decreasing bubble size and pH. As for the influence of particle size, it was found that as particle size increases, collection efficiency decreases for weakly hydrophobic samples but increases for strongly hydrophobic samples. Under experimental conditions where the stability and attachment efficiencies equal unity, various collision efficiency models were tested against the experimental flotation data.

The Ultrasonic Dissolution of Aqueous Colloids

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Ultrasonic waves are sound waves which lie in the frequency range of >16 kHz to 500 MHz. When ultrasound is generated in an aqueous solution, absorption of the sound waves occurs via the formation of tiny vapour/gas filled microbubbles or cavities. The eventual implosive collapse of these cavities leads to the production of a great deal of turbulence in the bulk liquid. More importantly, however, bubble collapse also leads to localised increases in temperature and pressure great enough to lead to the homolysis of water molecules and the production of the highly reactive hydrogen and hydroxyl radicals. These radicals either recombine or react with solute molecules which can disperse into the bulk solution, leading to further chemical processes[1]. It has been shown that, due to these chemical effects of ultrasound, colloidal metal sulphides and oxides may be dissolved in solution[2, 3]. The efficiency of the dissolution process was found to depend on the presence of certain chemical additives in solution and on a number of physical parameters, some of which shall be discussed.

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A Sims And XPS Investigation Of Water Plasma Modified Aluminium Oxide Surfaces

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Surface hydroxyls are the principal reactive sites involved in monolayer adhesion and bonding on oxide surfaces. In most cases determination of these groups has involved high surface area (usually several hundred $\text{m}^2 \text{g}^{-1}$) powders using spectroscopic techniques such as FTIR and NMR. Yet most studies of molecular adsorption and subsequent formation of thin film coatings involves much lower surface area substrates (eg. flat plates).

In this work a combination of X-ray photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) have been used initially to examine hydroxyls (silanols) on low surface area crystalline aluminium surfaces.

This involved various substrate pretreatments both in and ex situ prior to analysis including long term water plasma (maximum hydroxylation) and inert gas ion bombardment in ultra high vacuum (UHV) [1]. Relative hydroxyl concentration levels were examined using XPS, quadrupole and TOF static Secondary Ion Mass Spectroscopy

In XPS the speculative nature of the curve fitting of the broad O1s peak for silanols highlighted the limitations of the technique even in the angle dependent mode at shallow angle (increased surface sensitivity approaching that of static SIMS). A quantitative reference for the SIMS was therefore at best only speculative. Comparisons with literature values of silanol concentrations from surface crystallographic considerations and/or data derived from powder studies was also examined. Plots of positive ion and negative ion ratios at the various stages of hydroxylation were correlated with XPS analysis.

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Comparison of Bauxite Residue Suspensions

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The presentation gives an overview on the rheology of bauxite residue from refineries in Australia, Jamaica, Surinam, Brazil and the USA. The samples are compared in terms of their shear and compression properties. Synthetic residue samples prepared from the digestion of bauxite are also compared to those obtained from industry. The differences in flow properties are related to physical and chemical differences between the various samples. The samples are then compared on an even basis by removing some of the chemical and physical differences. Finally the realisation is made that many of the samples are identical in terms of their rheological properties.

Growth of Crystalline Zinc Sulfide Thin Films by Single Source Chemical Vapour Deposition

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Zinc sulfide, a II-VI transparent semiconductor material, is of interest due to its potential applications in the optics industry. Its properties include a wide band gap (~3.65-3.80eV), photoconductivity, electroluminescence and piezoelectricity. Thin films of zinc sulfide have been used extensively for blue light emitting diodes as emitting layers and electroluminescent displays. Chemical Vapour Deposition (CVD) is an attractive technique for producing high quality films suitable for device applications. CVD methods utilising separate zinc and sulfur sources have been used to prepare zinc sulfide films. In this work the "Single Source CVD" method was investigated for the growth of ZnS films. A "single source precursor" contains both the zinc and sulfur elements in the same molecule. Zinc diethyldithiocarbamate $Zn[(C_2H_5)_2S_2CN]_2$ was examined as a potential single source precursor.

Preliminary work indicates that crystalline thin films of zinc sulfide can be grown on various silicon based substrates such as Si(100), Si(111) and corning 7059 glass where the substrate temperature ranges from 250 to 450°C. At a substrate temperature of 420°C, the films grown on silicon displayed either cubic (Sphalerite) or hexagonal (Wurtzite) polymorph structures while films deposited on corning glass was amorphous. Higher substrate temperatures were required to produce crystalline films on the corning glass. The crystallinity of the films were examined by x-ray diffraction, the interface was studied by x-ray photoelectron spectroscopy and the important optical properties determined by ultraviolet/visible spectrophotometry.

Mechanism of Scale Formation in Bayer Liquors

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The fundamentals of aluminosilicate scale on Bayer Plant heat exchangers have been studied to gain an insight into the mechanism of scale formation. The two phases of scale present on heat exchangers are sodalite and cancrinite. Cancrinite is hexagonal and sodalite is cubic. The unit cell parameters for cancrinite are $a=12.67\text{\AA}$ and $c=5.18\text{\AA}$. For sodalite the parameter is $a=8.89-8.98\text{\AA}$. The solubilities of each phase of aluminosilicate have been obtained and the kinetics of scale formation have also been studied. The solubility of cancrinite has been found to be 0.13g/L SiO_2 at 90°C rising to 0.28g/L SiO_2 at 220°C. For sodalite the solubility decreases slightly from 0.16g/L SiO_2 at 90°C to 0.14g/L SiO_2 at 120°C then rises to 0.28g/L SiO_2 at 220°C. The decrease in solubility is due to a phase change from sodalite to a less soluble cancrinite. This phase change is essentially complete by 180°C and the solubility of the initial sodalite seed is that of cancrinite seeded solutions. These results show that the rate of phase transformation is temperature dependant. The kinetics of scale formation have been studied to have a baseline in which to compare any seeded desilication experiments. This study was conducted over 4 hours in the temperature regime 90°C to 240°C. From 90°C to 160°C there was no appreciable reduction in silica concentration. From 180°C to 240°C the rate sharply increased indicating that kinetics play a greater role in the formation of scale than does thermodynamics. XRD analysis of scale formed show that sodalite is formed at 160°C and at 240°C cancrinite is the predominant phase present. Previous work has shown that sodalite scale forms first which then undergoes a phase transformation to cancrinite. The results show that this transformation at 240°C is very rapid but slow at 160°C. SEM analysis shows the morphology of the scale is 'cotton ball' like upto 160°C and pseudo-hexagonal at higher temperatures. All samples show formation at individual nuclei on the surface of the substrate and not a total surface coverage. Light scattering measurements of the Bayer Liquor show no colloidal material in the solution above 27nm in size proving that scale forms on the surface of the heat exchanger pipes and not in the bulk of the solution.

In Situ FTIR Investigation of Adsorption at the Metal Oxide / Aqueous Interfaces

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The investigation of adsorption of species from aqueous solution onto metal oxide surfaces and the determination of the mode of surface binding is of particular interest in both natural and technological systems.

In situ studies of adsorption on metal oxide sol-gel films from aqueous solution have been carried out using Attenuated Total Reflectance (ATR) FTIR spectroscopy. Thin metal oxide films are prepared by evaporation of a small volume of metal oxide sol on a ZnSe ATR prism surface(1). Oxides investigated include TiO_2 , ZrO_2 , Al_2O_3 and Ta_2O_5 . Dilute adsorbate solutions are placed in contact with the oxide gel films and difference spectra, with respect to H_2O on the films are recorded.

It has been shown, by comparison of the infrared spectra of known co-ordination complexes, that typical chelating ligands bind to these oxide films in a bi-dentate fashion (1). Surface binding equilibrium constants for various adsorbates have been evaluated using the Langmuir isotherm(2). Co-ordination of bidentate ligands from aqueous solution is coupled with the loss of surface adsorbed carbonates. These carbonates originate from the reaction of atmospheric CO_2 with the hydrous oxide surface during the gel-drying process.

Zirconium dioxide films dried in a CO_2 atmosphere show enhancement of the carbonate bands(2). Assignment of these bands indicate the presence of bicarbonate and bidentate carbonate surface species. Adsorption of bicarbonate ions from aqueous solution form bidentate carbonates on ZrO_2 sol-gel films(2). Isotopic labelling was used to assign bands associated with the surface carbonate species.

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A Comparison of Bonds Formed Between Epoxy Adhesive and Aluminium Pre-Treated with Phosphonate and Silane Compounds

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Organo-silicon coupling agents are ambi-functional compounds which can link chemically dissimilar materials. The typical structure is Y-Si(OR)_3 where Y is an organic ligand capable of interacting with an adhesive and R is usually a methyl group. In aqueous solutions the methoxy group hydrolyses and the silanol can then react with the metal oxide substrate(1). In contrast, phosphonate molecules are traditionally used as hydration inhibitors in industrial applications. The typical structure is $\text{N(CH}_2\text{P(O)O}_2\text{)}_3$. The phosphonate groups are ionised in dilute aqueous solutions and can form covalent bonds with the metal oxide(2).

In this study both classes of compound have been applied to aluminium adherends prior to the application of an epoxy adhesive from dilute aqueous solutions. The relative performance of each compound has been measured by monitoring the crack growth of adhesively bonded double cantilever beam specimens under mode I stress in a hydrothermal environment. FT-IR and XPS have been used to characterise the nature of the films adsorbed on the aluminium, as well as their relative ability to inhibit aluminium oxide hydration. Together with analysis of the failed test specimens, these results have been used to explain the relative performance of the compounds in the adhesive system and develop a simple model to explain bond strength degradation.

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The ACME Guide to Cheating with an AFM

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With the rapid increase in the number of publications involving AFM force measurements, scientists need to be aware of the subjectivity of the analysis procedure. Examples will be presented in which different results can be obtained from the same data by less than scrupulous analysis techniques. Guidelines for the presentation of AFM force data are suggested.

Particle-Particle Interactions Using Atomic Force Microscopy and Rheology Measurements

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An Atomic Force Microscope was used to investigate the effect of polyelectrolytes on the interparticle forces present in a simplified model sludge system. The effect on the rheology (or treatability) was monitored using a vane rheometer to obtain shear yield stress measurements. The polyelectrolytes under investigation were 2k, 90k, 750k, and 4000k molecular weight poly(acrylamide) LT20. The model system was based in a SiO₂ (silica) suspension.

The PAA was shown to act as a dispersant, creating a steric barrier that stabilised the system. The effect was more pronounced for the lower molecular weight polymers. This steric barrier was only observed in AFM studies for the high molecular weight polymers. It was only observed at lower molecular weight due to the size of the interactions being of the order of the surface roughness and/or the adsorption of the polymer being weak.

The LT20, a non-ionic polyelectrolyte was shown to flocculate the system producing an increase in shear yield stress. This was attributed to an increased attractive force between the particles. A small steric barrier was observed in the AFM measurement but the large attraction, thought to be due to polymer bridging, was not observed. The anomaly has been attributed to the differences in technique, where the AFM is a dynamic measurement and the vane technique probes the slurry at close to equilibrium.

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Force measurements between oxide and sulphide surfaces using colloid probe microscopy

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Interactions between dissimilar surfaces control a vast number of biological and technological processes. In the sulphide minerals industry the flotation of valuable ore fractions is subdued by the adhesion of both natural and process derived particulate oxides [1]. This form of surface contamination reduces the attachment efficiency between minerals and bubbles inhibiting recovery. An atomic force microscope has been used to measure surface forces [2] between a single ZnS sphere and in experimental sequence mica, silica and the original mica surface in electrolyte at pH 5.8. The interactions were found to be monotonically repulsive for all separations including contact as confirmed by the absence of any adhesion. Surface potentials for ZnS, previously measured in symmetrical AFM interactions [3], were used in a nonlinear Poisson-Boltzmann equation [4] to obtain potentials for the oxide surfaces. Values for mica and silica, in 2×10^{-4} M NaCl, were -23 and -52 mV, respectively. Electrokinetic measurements revealed an isoelectric point between pH 7-8 for the synthetically prepared ZnS creating the expectation of an electrical attraction similar to that observed in dissimilar oxide/oxide systems [5,6]. It is believed that surface modifications are responsible for the anomalies in oxide/sulphide interactions.

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The Electrokinetics of Latex Particles Covered with Temperature Sensitive Hydrogel Layers

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Latex particles with temperature sensitive hydrogel layers were synthesised and analysed by Makino et al.[1]. Their work showed that a dramatic change in electrophoretic mobility occurs at the phase transition temperature of the hydrogel layers (33°C). At temperatures less than 33°C the layers are hydrated and extended. Above the transition temperature the layers become dehydrated and collapse onto the surface of the particle.

In this study, similar latices were synthesised and analysed using a range of electrokinetic measurements. Electrokinetic measurements were performed below and above the phase transition allowing information to be gained on the effect of such layers on electrokinetic behaviour.

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The Effect of Rheology on Coalescence Phenomena in Emulsion Systems

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The quality of some food and industrial products such as sauces, mayonaises and paints depends on the stability of the emulsion. In order for the rheology and stability to be properly controlled, an understanding of the properties that effect coalescence is necessary. This project involves the development of a technique "Imaging Ellipsometry" to the monitoring of the liquid/liquid interface of droplets as they coalesce. Imaging Ellipsometry will yield information on how the interaction and viscous forces affect the coalescence process, the interplay of these processes and how the rheological properties of the continuous medium affects this interplay. This technique will be employed to investigate both model and complex systems to determine whether the effect of altering the viscosity of the continuous phase is system dependent, or applicable to all emulsion systems.

A Spectroscopic Study of Polymers in Shear Flow Fields

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Polymer solutions show complex rheological behaviour. This behaviour arises from the solvent-polymer, polymer-polymer interactions and or the deformation and orientation of the polymer molecules in the shear field. Recent experimental interest has begun to focus on the measurement of the polymer conformation and the orientation changes in shear fields measured by light scattering and birefringence. The aim of this study is to use simple optical measurement of a polymer chromophore in well defined shear fields. The polymer chromophore is poly(4-butoxycarbonylmethylurethane Diacetylene) 4BCMU which shows distinct absorption anisotropy and changes in the wavelength of the absorption maximum with changes in the persistence length of the polymer. Using simple absorption measurements the degree of deformation and orientation of the polymer in the shear fields will be measured. The rheo-optical measurements are obtained for a range of concentrations and solvent composition using the Couette geometry. Verification of the extant theories relating measured flow behaviour to the polymer properties will thus be enabled.

The Relationship between Surface Chemistry and Rheology for both Symmetric and Asymmetric Colloidal Suspensions

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A critical relationship between the electrokinetic and rheological properties of concentrated colloidal suspensions has long been presumed. Until several years ago, however, techniques such as electrophoresis allowed quantification of electrokinetic surface properties only under extremely dilute conditions. The relatively recent advent of the electroacoustic technique of colloidal surface characterisation has allowed electrokinetic studies to be performed in concentrated colloidal suspensions [1]. Such concentrated conditions approach those native to techniques of rheological suspension characterisation, and thus allow more realistic comparison of electrokinetic and rheological properties.

In this study, electrokinetic and shear yield stress measurements have been performed on both a 'model' spherical alumina and a plate-like kaolinite aqueous system as a function of volume fraction. In addition, both systems have been studied as a function of electrolyte types, valances and concentrations, as well as the low molecular weight hydrophilic 'steric'-type additives identified by Leong *et al.* [2]. A selection of the most important of these results, and their ramifications on the surface chemistry - rheology inter-relationship, will be presented.

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Rheology of Aerosol-OT Microemulsions

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The rheology of water droplet and bicontinuous microemulsions of the widely used anionic surfactant sodium di (2,2,-)ethylhexyl sulfosuccinate (Aerosol-OT, or AOT) is examined. Previous studies have been conducted on the rheology of didodecyldimethylammonium bromide systems.¹ We are looking at the shear thinning on AOT systems which occur at shear rates greater than $10\,000\text{ s}^{-1}$. We have examined the effects of varying the oil in the AOT/water-in-oil microemulsion systems. In these AOT microemulsions we observed how droplet interactions and percolation effects cause changes in the zero-shear viscosity and the unusual shear thinning behaviour that results therefrom.

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Surfactant Enhanced Black Coal Dewatering

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Water, whilst being the work horse of coal beneficiation, causes a range of undesirable problems in the clean product. Reduction of this moisture leads to significant economic benefits and improved coal handling.

Surfactants have been shown to reduce the residual moisture of the clean coal product when used in conjunction with established mechanical dewatering methods. Puttock and Wainwright¹ postulate that to chemically enhance dewatering there must be a reduction in the surface tension (γ_{LV}) of the wetting liquid and an increase in contact angle (θ).

The interaction of anionic, cationic and non-ionic surfactants with coal of varying rank was investigated using contact angle, adsorption, interfacial tension and dewatering measurements. The effect of surfactants on coal surface hydrophobicity was investigated using the captive drop contact angle technique. An increase in hydrophobicity was observed upon addition of surfactants for the higher rank coals, however no change was evident for the lowest rank coal. Surfactant adsorption isotherms were measured using coals of varying rank, with adsorption density found to be inversely related to coal rank. Surface tension measurements on the surfactant solutions were performed using a FTA 200 Dynamic Contact Angle instrument. The effect of surfactants on the residual saturation (R_s) of coal slurries was investigated using centrifugal dewatering, with residual saturation able to be reduced significantly only for the highest rank coal.

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Adsorption of Organic Molecules on to Mineral Surfaces

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As part of a research program on the interaction of organic solutes with mineral surfaces, the adsorption of a polymer and two fluorescent dyes to the surfaces of kaolin and alumina has been studied. Remazol Brilliant Blue R adsorbs only weakly to alumina and kaolin and is therefore a suitable label for use in studies of adsorption of PVA to these minerals. PVA labelled with Remazol Brilliant Blue R has similar affinity for both alumina and kaolin surfaces, with Langmuir-like isotherms. On the other hand, 3,6-diamino acridine (proflavine) adsorbs to kaolin far more strongly than it does to alumina. Aspects of this adsorption, and attempts to end label polyethylene oxide chains with 3,6-diamino acridine to allow selective polymer adsorption, will be discussed.

Surface Adsorption of Detergent on the Wool Fibre Surface

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Detergents are used extensively in the chemical and physical processing of wool. However, little work has been done on the surface adsorption of detergents on the wool fibre surface. Previous methods used to analyse nonionic detergents have not been able to determine unequivocally whether the detergent is on the fibre surface. In this work, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (TOF-SIMS) have been used to directly detect adsorbed detergent.

The surface adsorption and diffusion of nonionic detergents on the wool fibre surface have been investigated using these surface sensitive techniques. Our results indicate that the detergent molecules remain adhered quite strongly to the fibre surface even after extensive washing in distilled water. This result suggests the possibility of a hydrophobic interaction between the covalently bound lipid on the fibre surface and the hydrophobic region of the detergent molecule. The sticking properties of detergent on fibres, where the bound lipid has been removed is currently being investigated. It will also be shown that the detergent molecules diffuse into the fibre surface under both ambient conditions and at raised temperatures. This result has implications in relation to the effect of storage time before further processing.

Effect of Polydispersity on the Crystallisation of Hard Sphere Colloids

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Sterically stabilised polymer particles suspended in non-aqueous solvents provide a hard-sphere system which can be made to undergo a disorder-order phase transition. Such suspensions provide insights into the process of crystallisation which are beyond experimental reach in atomic or molecular systems. The slow dynamics and large size of the colloidal particles permit time resolved light scattering studies of the crystal lattice as it emerges from the fluid. By studying the diffraction pattern, it is possible to monitor the amount, size and density of these crystals as they grow.

The effect of polydispersity on the crystallisation process is investigated by gradually introducing an increasing proportion of smaller than average particles to the suspension. The polymer composition of these additional particles is slightly different to that of the main component, presenting the opportunity to try and observe one component at a time. This is achieved by varying the temperature to selectively match the refractive index of the background suspension medium to one particle species.

These experiments reveal that crystallisation is slowed dramatically in a polydisperse system, lending weight to the conjecture that some compositional change is required at the crystal-liquid interface.

Single Particle Motions in Concentrated Colloidal Suspensions

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The self-diffusion of colloidal particles has been measured on concentrated suspensions with particle interactions approximating hard spheres. As the particle concentration of the colloidal suspension is increased, phase transitions occur, from a disordered to a crystalline state. By using a highly asymmetric mixture of polymer particles and silica of the same radius we measure, by Dynamic Light Scattering, single particle motions. This is done for metastable colloidal fluids whose equilibrium state is crystalline.

Evaporation Resistances of Octadecanol and Cholesterol

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The reduction in evaporative losses on a body of water is extremely important, especially in areas of drought and water shortage. It has been known for a long time that monolayers of certain long-chain amphiphilic molecules have the property of inhibiting evaporation. Possible explanations have been proposed in terms of the structure and orientation of the monolayer, phase transitions induced by surface pressure change, lattice re-arrangement following phase transition, and long-range and short-range forces involved in such a gas-liquid interfacial system.

Monolayers of octadecanol, cholesterol, and octadecanol-cholesterol mixtures are currently being studied in terms of its effect on evaporation resistances. It has been found that the straight long-chain alcohol of octadecanol produces monolayers of high evaporation resistance, whereas the non-linear chains of the cholesterol molecule results in monolayers of very low evaporation resistance. It has also been found that the presence of cholesterol in octadecanol mixtures can reduce evaporation resistance significantly. Techniques and equipment used include a film balance equipped with an evaporimeter, neutron reflectivity and X-ray synchrotron studies. It has been suggested that the two-dimensional structure of the monolayer affects the degree of evaporation resistance.

Interaction of Ions and Molecules with Phospholipid Monolayers and Bilayers

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Natural lung surfactant aids the contraction and expansion of the lung as we breathe. Many ions and molecules interact with the surfactant which affects the breathing mechanism.

Natural lung surfactant is made up of a complex composition of phospholipids, proteins and glycoproteins. The hydrophilic and hydrophobic character of phospholipids allows them to produce unique interfaces with the air and aqueous phases. These interfaces are being examined by a Langmuir film balance technique and by optical microscopy.

At this time results from both techniques are providing evidence of the interaction of ions, such as Ca^{2+} and Al^{3+} , and of molecules, for example, ascorbic acid with dipalmitoyl phosphatidylcholine.

Structural Effects of Yielding of Suspensions in Compression

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The compressive yield stress, $\text{Py}(\phi)$, is an important rheological parameter for the characterisation of concentrated flocculated suspensions. It is a measure of the compressive strength of inter-particle bonds in a fully networked suspension structure and is used in the design of processes for the dewatering of fine particle suspensions. Results from well characterised colloidal ZrO_2 and Al_2O_3 suspension systems are given showing the effect of flocculation conditions, sample preparation methods and the initial suspension concentration on the compression rheology. The structure of the suspension has been found to be dependent on these factors. Feasible explanations for these observed effects will be given.

Interaction Forces Measured between Silica Surfaces in Solutions of Polystyrene Sulphonate and CTAB.

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Interaction forces were measured between silica surfaces, onto which polystyrene sulphonate/CTAB had been adsorbed, using the Atomic Force Microscope. Previous studies have found that the adsorbed conformation is dependant upon the order of addition of PSS and CTAB. Hence, forces were measured under the following conditions.

- (1) Solution of polystyrene sulphonate and CTAB were equilibrated and then introduced into the apparatus.
- (2) CTAB was initially adsorbed onto the surfaces and polymer subsequently added to this solution.

A range of solution pH were investigated in both cases.

Effect of hydrophobicity of substrate on surface aggregate formation

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Recent work with the Atomic Force Microscope (AFM) has shown that surfactants at the solid/liquid interface do not necessarily form a smooth bilayer, as implied by early surface force measurements, but aggregates taking the form of either hemicylinders or hemimicelles. Using a combination of the AFM and Measurement and Analysis of Surface Interactions and Forces (MASIF) it is possible to look at adsorption as a function of hydrophobicity. Surface force measurements have been made between glass surfaces in CTAB at different pH levels. These have shown that there is less adsorption in more acidic solutions, where the competitive adsorption from hydrogen ions is greater. Further surface force measurements and Atomic Force Microscopy show the effect that the reduced hydrophobicity of the monolayer have on the type of bilayer that forms.

Molecular Modelling of the Adsorption of Sulphonated Naphthalenes onto Graphite Surfaces

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Semi-empirical Molecular Modelling techniques have been used to investigate the interaction between sulphonated naphthalene derivatives and graphite surfaces. Adsorption is examined via the heat of reaction and changes in the position of the surfactant molecule. Results are discussed in comparison with previous experimental conclusions.

Electroacoustic and Dielectric studies of the coating process of TiO₂

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Electroacoustics and dielectric response measurements have been used to study the surface deposition of alumina and silica onto titania. The adsorption of these ions result in the formation of a protective oxide layer and inhibits the reduction of bare titania by UV radiation as well as improving its stability in aqueous media.¹

When an alternating electric field is applied to a colloid, sound waves are generated which depend on the applied frequency, the particle size and on the zeta potential. This is known as the electroacoustic effect.² By following the change in zeta potential with electroacoustics, we are able to monitor the deposition of alumina and silica in concentrated titania slurries. The information obtained shows that as the metal oxide coats titania, the isoelectric point of the titania surface changes to that of the metal hydroxide.

O'Brien has also shown³ that the double layer around a particle adjusts to a change in the applied field producing an alternating dipole, S . Over the megahertz frequency range, the permittivity, ϵ , of the suspension changes and this can be related to the complex conductivity, K^* , of the medium. From this, the surface conductance, K_s of the colloid can be calculated. By relating the change in permittivity of the uncoated particle to the coated particle, the coating thickness may then be obtained.

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Reversible Surface Wetting And Particle Adsorption

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It is believed that stimuli such as light, pH and redox potential can induce reversible wetting on "smart coated surfaces". The coated surfaces will consist of thin organic films grafted predominantly onto silica and quartz (whether it be as flats, capillaries, cylinders or spheres). Initially, organic films containing long alkyl chains terminated at one end by a siloxane or silyl ether linkage to a surface and at the other by a pyrimidine molecule will be investigated. Under the action of UV radiation, photodimerization of the pyrimidine can result. With an understanding of monomer and dimer pKas together with the knowledge of enhanced dimerization in an ordered state, reversible wetting should be observed. Similarly, simple pH sensitive wettability can be induced by replacing the pyrimidine with ionizable groups such as carboxyl or amine groups and adjusting the pH of the surrounding phase. Furthermore, conducting polymers like poly(alkylthiophenes) could be anchored to the surface and the redox potential varied with the use of oxidants and reductants to observe reversible wetting. In parallel, it is intended to study small particle adsorption / desorption on these surfaces as a range of forces can be explored (i.e. DLVO and hydrophobic forces) by altering the nature of the surface (eg. positive surface, negative particles, no hydrophobicity and variations thereof). Surface characterization using a number of techniques including AFM, FTIR and XPS will be performed while the wetting behaviour will be probed by a sensitive Wilhelmy plate technique over a wide velocity range. With this information, it is intended to build a model of the wetting behaviour which will ultimately provide an insight into the workings of a capillary pump together with controlled particle adsorption and release.

Foam Stability and pH Changes During Foam Formation

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The stability of foam produced using sodium dodecyl sulfate (SDS) titration column and the drained liquid during the foaming process, measuring the weight of foam collected as a function of time, and measuring the concentration of SDS and/or DA (following flotation) in the solution left in the flotation column, in the foam, and in the liquid drained from the foam.

The pH behaviour was particularly interesting, with a lowering in pH being observed in both the solution left in the flotation column following flotation, and the solution drained from the foam. Atmospheric carbon dioxide appears to play a role in this decrease in pH since the decrease was considerably smaller when flotation was performed under nitrogen (there was, however, still a decrease in pH under these conditions).

The "stripping" of surfactant out of solution and into the foam will be discussed, along with the origin of the decrease in pH (which is currently not fully understood).

A Study of the Surface Structure and Reactivity of Metal Oxides

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The reactivity of oxide surfaces in solution has been studied extensively for many years. The overall objective of this study is to determine the factors controlling the reactivity and dissolution of the semiconducting cobalt monoxide (CoO) and nickel monoxide (NiO) surfaces for comparison with ionic magnesium oxide (MgO) surfaces. Specifically, this work will examine the reactions of these oxides in acid, alkali and neutral conditions. The mechanisms and factors controlling adsorption, reconstruction, dissociation etc. will be examined by a solid state chemistry/surface science approach. Both oxides are p-type semiconductors due to non-stoichiometry however the dissolution of CoO is several orders of magnitude higher than NiO at low pH. Factors considered important to dissolution such as electronic behaviour and surface defects of these oxides are currently being researched. The main scope of this work is based on theoretical calculations of oxide surfaces using quantum mechanical codes. The semi-empirical code SINDO1 is currently being used for the investigation of surface relaxation, vacancies and adsorption at CoO and NiO surfaces. The oxide surface is represented by an embedded cluster. In addition, AFM and STM will be used to provide topographical information on surface defects as well as surface reconstruction in aqueous solutions.

Surface Characterisation of Mixed Oxides

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The formation of mixed metal hydroxides is part of the synthetic pathway to the formation of various metallic containing compounds. For example, superconductors, ceramics and a range of metallic oxide catalysts are all based upon the generation of mixed hydroxides as part of their formation process. Another important factor in the characterisation process is to gain an understanding of parameters which influence the removal of metals from solution. An increased understanding of precipitation, coprecipitation and adsorption processes, which are currently utilised to remove toxic heavy metals from solution, may enhance the efficiency of these purification procedures in the environment.

The specific metals of interest in this study are Fe(III), Cr(III), Ni(II), Zn(II) and combinations of these for coprecipitation studies. Variation in conditions during the precipitation / coprecipitation process can alter the structure and surface properties of the solid, and as a result, influence the overall nature of the particle. A series of both pure hydroxides and binary hydroxide coprecipitates formed over a broad range of molar ratios have been prepared by forced hydrolysis from solution. The removal profile for several of the systems under investigation has been examined as well as desorption characteristics for a given complex. Several techniques have been used to quantify the physical and chemical properties of the formed particles. These include the in situ measurement of the amorphous hydrous oxide particle size. Gas adsorption isotherms as a means of estimating the BET surface area and pore size distribution of the dry colloid. Fourier transform infrared spectroscopy has also been utilised to provide information on the dried product.

Spectroelectrochemistry of Colloidal Silver

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The spectroelectrochemical response of small silver particles was studied in aqueous solution using an optically transparent, thin layer electrode. The position of the surface plasmon band of colloidal silver was found to depend on the applied electrode potential. A value of $80 \pm 10 \mu\text{Fcm}^{-2}$ was obtained for the double layer capacitance of the silver-water interface based on the spectroelectrochemical shift. The equilibration kinetics of the particles with the electrode obeyed the Cottrell equation. However, the number of electrons transferred at each particle-electrode encounter was found to be potential dependent, and reached 1600 ± 400 at potentials more negative than -0.4V vs Ag/AgCl . The evidence suggests that this particle charging current occurs via electron tunnelling across the particle and electrode double layers. Changes in the redox potential of the particles due to added chemical reductants could also be directly monitored by laser doppler electrophoresis.

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Bubble Bubble Nucleation and Growth in Solutions Supersaturated with a Gas

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Nucleation and growth is of significance in nature and in a variety of multiphase processes. The focus of the present investigation is the physics and the physical chemistry of a forming bubble, and the frequency of the cycle of bubble production in solutions supersaturated by a gas, as occurs in carbonated beverages, or even in dissolved air flotation. Experiments were carried out to observe bubble nucleation, bubble growth, and site deactivation mechanisms under degassing of a solution supersaturated with gas on single sites in a glass surface. They were performed on a solution of water supersaturated with carbon dioxide. These mechanisms were filmed using a CCD camera as the concentration of carbon dioxide decreased. The results showed that mass transfer, rather than the classical nucleation theory, provided a quantitative account of bubble production at a surface for solutions supersaturated with gas. The cycle of production depends on a bubble growth time t_g , and a nucleation t_n . A relationship between bubble growth time and the nucleation time was established. The relevant parameters for bubble formation from cylindrical cavities were determined to be the wetting depth of the liquid inside the cavity and the diameter of the bubble upon detachment.

POSTER SESSION B

Application of TOFSIMS to in situ analysis of the surface and sub surface region of individual mineral grains in coal

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Coal contains significant amounts of mineral matter which is generally undesirable in coal utilisation. A thorough understanding of its mineral matter occurrence in coal is therefore critical.

In this work, time-of-flight secondary ion mass spectrometry (TOFSIMS) is used to examine in situ individual coal mineral grains, eg quartz and other mineral species. Successive depth profiling (with a Ga ion beam) of a small area (~200 μm^2) on discrete mineral particle surfaces provides elemental and chemical concentration depth profile through a thin (50Å) surface layer.

Secondary ion imaging has been used to measure the lateral distribution of associated elements across 10 micron particles embedded within the coal. Both experiments clearly show the elemental and chemical composition on mineral particle surface which is very different from that in sub-surface layer.

Analysis of Hollow Fibre Liquid Membrane Designs for Cr(IV) Removal in Electroplating Rinse Waste

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Small industrial electroplating companies are under increasing pressure to reduce waste by recovery. In the electroplating process, after the metal is plated it is rinsed in a bank of counter-current rinse baths. The chromium level in the rinse baths builds up over a period of time. The baths' rinsing becomes so inefficient it requires replacement. Electrolysis, ion exchange and precipitation techniques have been used to treat the rinse baths' waste. These techniques cannot exclusively recover ions and are used as end of pipe applications, creating more wastes than were originally processed. This work discusses the design of hollow fibre liquid membrane modules to recover and concentrate the chromium from the electroplating rinse baths for recycling.

ATR Spectroscopy of Metal Ion Extraction

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Solvent extraction methods are widely used in the hydrometallurgical industry for the separation and purification of metals. The technique involves contacting an aqueous liquor containing a variety of metal ions with an organic phase containing a reagent which will complex with one or more of the metal ions in solution, but not all, and preferentially solubilizing the complex in the oil phase, thus achieving separation and purification.

In recent years, the technique of attenuated total reflection (ATR) spectroscopy has been adapted to the liquid-liquid interface to understand the kinetic parameters which influence the extraction of a metal at a oil-water interface.

The aim of this research is to modify the ATR spectroscopy technique to enable a study of the kinetics of extraction of Cu^{+2} by 7-(4-ethyl-1-methyloctyl)8-hydroxyquinoline (Kelex 100), at the oil-water interface. The interfacial concentration of the Copper-Kelex 100 complex formed as a function of time, under different conditions, is monitored by ATR spectroscopy as the reaction proceeds.

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Effect of the Substrate Temperature on the Preferred Orientation of ZnO Films Grown by Single Source Chemical Vapour Deposition

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Single Source Chemical Vapour Deposition offers a simple method for the growth of high quality zinc oxide (ZnO) films. ZnO is a wide bandgap semiconductor with a high piezoelectric coefficient. The application of ZnO films in devices depend on a number of properties in the films such as a preferred c-axis orientation and a low level of contamination.

This study examines some the factors in the growth of highly c-axis oriented films. In particular the importance of growth temperature in determining the composition, crystal structure, preferred orientation and morphology of films. Films were grown on Si(100) substrates at range of temperatures and the properties of the films produced examined in detail. The chemical composition of the films produced was characterised using X-ray Photoelectron Spectroscopy. X-ray Diffraction was used to examine the crystallographic properties and Scanning Electron Microscopy provided information on the morphology. X-ray Absorption Spectroscopy (NEXAFS and EXAFS) data will also be presented.

It was found that although the growth temperature has some effect on the composition, the greatest influence was on the crystallographic properties and morphology of the films produced. Films with a range of crystallographic structures and morphologies can be produced by a relatively small variation in temperature.

The Fragmentation Reaction of Basic Zinc Acetate on heated Si(100)

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The fragmentation reaction of $Zn_4O(\text{acetate})_6$ (basic zinc acetate, BZA) is of interest for the growth of ZnO films from single source chemical vapour deposition (CVD). Mar et al. [1] have shown previously, that BZA can be used as a precursor to grow ZnO films. Only when the deposition is performed in a water ambient a poly-crystalline, c-axis oriented film is grown at growth rates of ~ 500nm per hour.

To further understand the decomposition reaction that occurs on the heated substrate, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) have been used to investigate the early stages of film growth from a BZA precursor in the absence of water on Si(100). As demonstrated in earlier work [2], some oxidation of the Si substrate occurs at the substrate to film interface. The precursor fragmentation initially proceeds via an decarboxylation of the ZnO 'core' structure in the precursor molecule. This 'core' structure remains intact at a substrate temperature of 400°C. The fact, that no preferred orientation of the adsorbate film is found is explained by the incorporation of precursor fragments into the film and their chemical reaction with the Si substrate to form a mixed Si-ZnO-organic fragments interfacial layer.

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Characterisation Of Ultrasonically Initiated Polymerisation

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Synthetic latices are an important component of modern materials, finding application in products such as films, coatings, adhesives, textiles and paints. The synthesis of latex materials involves the free-radical polymerisation of a monomer which generally requires an added free radical initiator. Under ultrasonic irradiation and the resulting stable (resonant) cavitation, the monomer becomes the source of these free-radicals, eliminating the need for the added initiator. At this stage the initiation, propagation and termination steps are not clearly defined. The work covered so far has concentrated on the rate of free radical formation. These rates of initiation are being estimated by trapping the free radicals formed as a result of cavitation using DPPH, a free radical scavenger. Variables such as ultrasonic power, vapour pressure and concentration of monomer analogue are being investigated and compared with measured rates of polymerisation

Stability of Intralipid Emulsions

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Intralipid is a commercially available emulsion, containing 10% soybean oil and 1.2% of a naturally occurring phospholipid, egg lecithin. The aim of this study is to look at the stability of intralipid emulsions, prepared on a laboratory scale, by analysing the residual, aqueous-phase, surfactant concentration. Such laboratory preparations use either lecithin or a combination of SDS and DA as the active surfactant phase.

The stability of intralipid batches made in the laboratory is affected by factors such as the type of oil and surfactant used, the temperature at which the surfactant is added to the oil phase, the pH the coarse emulsion is adjusted to, and the number of times the coarse emulsion is passed through a microfluidiser.

To assess emulsion stability, a number of techniques can be used. Here, centrifugation, freeze thaw and autoclaving are used to stress the emulsions; whilst pH over time, particle size, visual inspection and residual surfactant concentrations are used to monitor emulsion stability. Such tests reveal that the average emulsion droplet size of 300 nm is remarkably robust and gives monodispersed, unimodal data. However, these results are not always consistent, leading to the requirement for a criteria, or protocol, for the acceptance and refusal of particle size data.

Emulsions synthesised with SDS and DA mixtures can be analysed for the concentration of both surfactants (individually), using a well developed two-phase titration method and the results correlated to emulsion stability.

Effect of pH on the Rheological Properties of Colloidal Alumina Dispersions

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The influence of pH on the rheology of colloidal alumina dispersions was investigated with four Al_2O_3 particle sizes at various solid concentrations. Nitric acid and potassium hydroxide were used for controlling the pH and the colloidal state of the dispersions. The alumina dispersions exhibit a wide range of rheological behaviour depending on the colloidal state, i.e., the degree of dispersion or flocculation. Maximum yield stress and viscosity occurred at or near the isoelectric point (IEP), where the dispersions are highly flocculated. At low or high pH, where the magnitude of the electrophoretic mobility of the alumina is high, a well dispersed low viscosity dispersion was obtained. Extreme sensitivity with pH was observed, whereby the dispersion viscosity can be changed by as much as two orders of magnitude with pH variation at constant volume fraction. In addition, the suspensions dispersed with base have higher viscosities than those dispersed with acid. This investigation also examined the effect of particle concentration and size on the rheological properties of Al_2O_3 dispersions. The result shows more pronounced concentration dependence of the maximum yield stress at high particle volume fraction. At the IEP, a power law can only represent the relationship between yield stress and particle volume fraction at a limited of solid concentrations.

Dynamics of Film Formation

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Acrylic acid is a hydrophilic stabiliser. When added to a butyl methacrylate emulsion it forms a "hairy" layer around the butyl methacrylate latex particles. Annealing the latex dispersion above the minimum film forming temperature of the polymer allows the particles to interdiffuse such that a mechanically continuous film is formed. Both nascent and annealed films have been examined using Atomic Force Microscopy. The effect this stabiliser has on film formation will be discussed.

Selective Flotation of Metal Cations: Effect of Macrocyclic Complexation

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The binding of cations, particularly metal cations to anionic surfactant films at the air/water interface has been studied using ion flotation to assist in the fundamental understanding of the interactions that occur at this surface. Results indicate that minimal selectivity exists at the air/ water interface for the alkali and alkaline earth metals.

The encapsulation of metal ions by macrocyclic ligands as an aid to ion flotation was also examined. This application was found to alter the flotation selectivity from the native selectivity of the surfactant to the selectivity of the macrocycle. This indicated that a surfactant/complex co-assembled film was being formed at the interface, which was also verified by surface tension measurements.

Surface and Electrochemical Studies in the Selective Flotation of Copper and Arsenic Minerals

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The increasing complexity and dissemination of new sulphide ore bodies generally means that a higher through-put of new ore has to be processed to achieve the targeted out-put of valuable minerals. The penalty element impurities that are commonly associated with sulphide ore bodies, such as arsenic, antimony, bismuth and mercury are then enriched with the valuable minerals in the flotation concentrate. These penalty elements are environmentally hazardous and have a detrimental effect on the physical properties of the metals with which they are associated. If the levels of these penalty elements exceed about 0.2% in the concentrate, hefty financial penalties are imposed by the smelters to remove these impurities. The penalty element minerals float with the valuable minerals because of their similar flotation behaviour and our lack of understanding of the processes that control their flotation. Therefore the aim of this research project is to conduct extensive surface and electrochemical studies on the copper-arsenic minerals of enargite ($\text{Cu}_3\text{As}_4\text{S}_{13}$) and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), to compare these with similar studies on the copper minerals of chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), covellite (CuS) and chalcocite (Cu_2S) and to devise procedures by which selective flotation may take place. Results of zeta potential measurements on the above natural minerals and synthesised enargite and tennantite samples, under different conditions, will be discussed.

The effect of particle surface coatings on the adsorption of orthophosphate using Sedimentation field-flow fractionation.

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The adsorption behaviour of pollutants to natural colloids is important in determining their fate and effect in the aquatic environment. These adsorption processes are affected by surface coatings such as iron oxide, manganese oxide and natural organic matter (NOM) which occur at the surface of aquatic colloidal particles. Sedimentation field-flow fractionation (SdFFF) was used to determine surface adsorption density distributions (SADD) for ^{33}P labelled orthophosphate onto suspended Chaffey Dam (NSW) colloidal samples. The surface adsorption density (SAD) is the amount of pollutant adsorbed per unit area of particle surface.¹ For a homogeneous particle samples, the SAD is expected to be constant. The SAD for the Chaffey sample was nonconstant which may be due to changes in particle shape, mineralogy or the nature of the surface coatings. Scanning electron microscopy (SEM) was used to determine particle shape by examining separated fractions.² The SAD was shape corrected using recently developed theory.³ Analysis of the Chaffey sample suggested changes in particle shape did not influence the SAD significantly. In light of the SEM analysis it was more likely the nonconstant SAD was associated with a change in mineralogy or surface coating composition. The purpose of this work was to investigate the effect of these surface coatings on orthophosphate adsorption. The particle surface coatings were selectively removed from the colloidal particles and the effects on orthophosphate adsorption was investigated.

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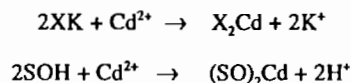
Cadmium(II) Adsorption on Kaolinite, a Two Stage Process

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In this study the adsorption of Cd(II) onto the clay mineral kaolinite has been investigated as a function of pH and Cd(II) concentration. The Cd(II)/kaolinite adsorption edge shows that the adsorption process occurs in two distinct stages, with a plateau appearing in the adsorption edge between pH 5 and pH 7. Constant pH experiments were used to study adsorption in each stage. pH 5.50 was selected for the study of adsorption in the initial stage, whilst pH 7.50 was used for the investigation of adsorption in the second. Adsorption isotherms at pH 5.50 could be modelled using a simple Langmuir equation. A multi-site model was required to fit the data at pH 7.50, and of the possible multi-site models the two-site Langmuir equation was selected. Potentiometric titrations were also used to characterise this adsorption system, with the titration data modelled using a constant capacitance surface complexation model. Both the surface complexation and Langmuir modelling strongly suggest that Cd(II) adsorption on kaolinite occurs initially, at low pH, as an ion exchange process on the permanently charged sites of the crystal face. At higher pH, beyond the plateau region in the adsorption edge, adsorption involves the formation of surface complexes with edge hydroxyl groups. Thus the following adsorption reactions are postulated:



where X- is a permanent charge site on the crystal face, K+ is a potassium ion from the background electrolyte, and SOH is an edge hydroxyl group.

Thermogravimetric and Differential Thermal Analysis (TG-DTA) of Australian Coals

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Coal is just one of the carbon based materials, that under certain conditions, can spontaneously combust as a consequence of its exposure to atmospheric oxygen. The oxidation of coal is a surface phenomena and it is an irreversible exothermic reaction that increases in tendency with increasing temperature.

Thermogravimetric and differential thermal analysis (TG-DTA) has been used to study the combustion profile of a series of Australian coals under different environments and conditions. These conditions include changes in atmosphere (static and dynamic) and changes in heating rate. The effect of surface modification additives (surface active agents) on the TG-DTA profile has also been studied.

Two coal samples, specifically Balmural and Buxtress (from the Drayton mine) have exhibited an unusual TG response. These coals display an increase in mass just prior to the onset thermal decomposition. This effect may be attributed to the chemisorption of molecular oxygen onto the surface of the coal prior to decomposition.

Study of the Extraction Kinetics of Nickel by LIX 84

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Solvent extraction is an important separation process that is used in a variety of industries. Until recently the majority of the research on extraction systems has been based on the equilibria of the system. If study is extended to the reaction kinetics, then a far larger variety and better separations are possible, encompassing better selectivity.

The majority of extractants that are utilised are interfacially active and almost totally insoluble in the aqueous phase. As a result the reaction of the metal ion and the extractant in most cases occurs at the interface. To follow and determine the kinetics of such a reaction, the static transfer cell using attenuated total reflectance (ATR) spectroscopy was developed to overcome some of the problems associated with other methods in use. Using the ATR static transfer cell, and stopped flow measurements with a micelle model system, the kinetics of the extraction of nickel by the active ingredient in LIX 84, 2-nonyl-5-hydroxyacetophenone oxime, was studied.

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SURFACE CHARGING MECHANISMS OF SOLIDS IN CONTACT WITH NONPOLAR LIQUIDS

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A nonpolar liquid is characterised by its very low dielectric constant, resulting in weak electrolyte ionisation, and in turn exceedingly low ionic strength and large Debye length. While the charging mechanisms of solids in aqueous media are well understood, our knowledge of charging between solids and nonpolar liquids is limited. A better understanding is desired to resolve the controversial topics in colloid science such as the contribution of electrostatic forces to colloidal stability, the validity of the Poisson-Boltzmann equation, and the applicability of DLVO theory in nonpolar media, and to safely deal with electrostatics in electric power and petroleum processing industry. Hitherto, a few mechanisms have been proposed, which attribute charging respectively to ion adsorption, acid-base interaction between the dispersed particle and the polymeric dispersant, or to electron transfer between the solid and the liquid as analogous to contact electrification between two solids. However, these mechanisms are largely based on a limited number of individual studies, and not accepted universally. In this project a Surface Force Apparatus (SFA) will be used to investigate possible electrical double-layer forces in liquids of low polarity, and hence to explore charging mechanisms. The effect of the presence of water, and some dissociation-promoting additives such as inverse micelles, triple ions, and crown ethers will also be considered.

Surface Studies of Organics in Coal

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Coal is an extremely complex organic substance, made more complicated by the presence of inorganic mineral matter. For many applications eg. power generation and metallurgical coke production the coal must be cleaned before it can be used. Many cleaning processes involve the use of water. Other methods, particularly with regard to fine coal beneficiation, involve the use of oil or other chemicals. In these processes, the hydrophobic nature of the surface of the coal is an important factor in the cleaning process. An understanding of the chemical composition of coal surfaces would thus greatly aid the development and improvement of new and existing coal preparation processes.

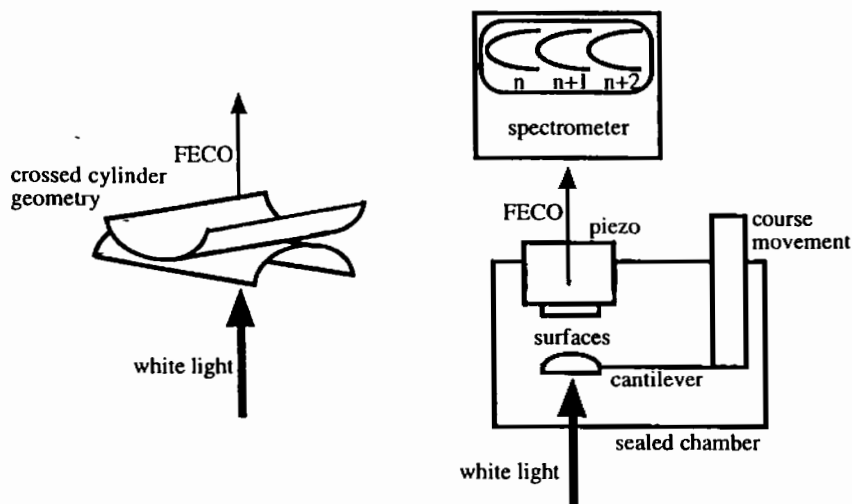
It is hoped that surface science techniques such as time-of-flight secondary ion mass spectrometry (TOFSIMS) and X-ray photoelectron spectroscopy (XPS) will enable the surfaces of different coals to be characterised. TOFSIMS was chosen because of the ability to detect high mass organic fragments, of which coal is primarily composed. Various coals, both unoxidised and oxidised, have been examined using ToFSIMS to determine any differences in the organic constituents of the coal surfaces.

In addition, initial work using polystyrene (as an model for organics in coal) has indicated that ToFSIMS will indeed be effective in the detection of relatively high mass organic fragments. However, sample preparation appears to be of crucial importance to the entire process, due mainly to the non-conducting nature of the materials being examined. Some preliminary ToFSIMS results will be presented.

EXPERIMENTAL TECHNIQUES

SURFACE FORCE APPARATUS

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



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

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

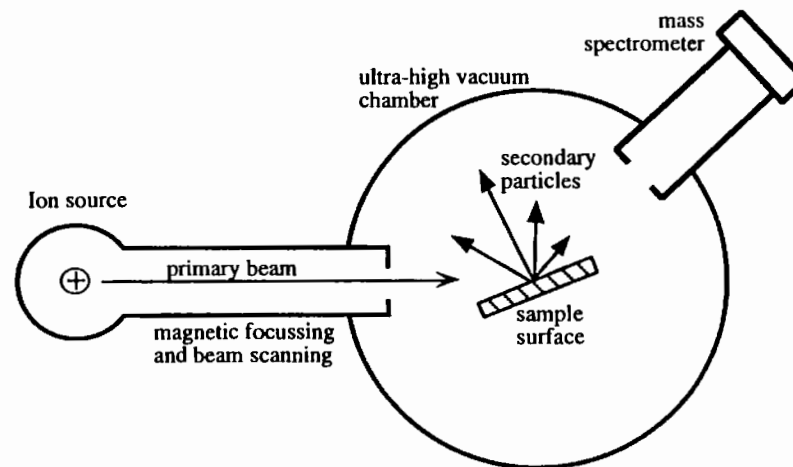
The crossed cylinder geometry approximates well as a sphere, with a radius equal to the geometric mean curvature of the two cylinders, interacting with a plane. Surfaces are restricted to those that can easily form transparent, thin smooth films, *e.g.* silica, sapphire, mica. Alternatively the interferometer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

Suggested reading

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

SECONDARY ION MASS SPECTROSCOPY

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



A (very) simplified schematic of a SIMS setup.

Primary beam species useful in SIMS include Cs^+ , O_2^+ , O^+ , Ar^+ , and Ga^+ at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm. The bombarding primary ion beam produces monatomic and polyatomic particles of sample material and resputtered primary ions, along with electrons and photons. The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV. The SIMS primary ion beam can be focused to less than 1 micron in diameter. Scanning where the primary ion beam strikes the sample surface provides for microanalysis, and the measurement of the lateral distribution of elements on a microscopic scale.

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

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

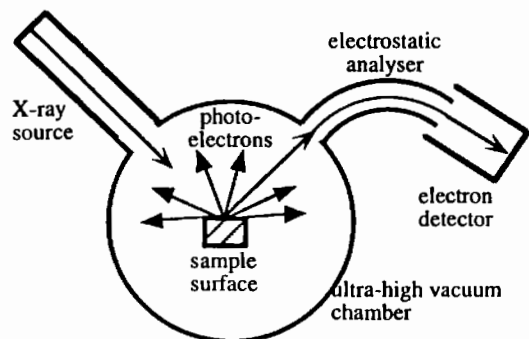
Mass spectrometry not only provides isotopic discrimination, but both negative and positive species can also be analysed.

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X-RAY PHOTOELECTRON SPECTROSCOPY

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



Schematic of XPS setup

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

$$KE = h\nu - BE$$

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

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

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