

FOURTEENTH
AUSTRALIAN
COLLOID AND SURFACE CHEMISTRY

STUDENT CONFERENCE

ALBURY, N.S.W.

AUGUST 1988



Thomas W. Healy



Robert J. Hunter

PREFACE

This meeting marked the twenty first anniversary of the Student Conference so it was, in many respects, a very special occasion. Our Melbourne University hosts, under the guidance of Franz Grieser went to enormous pains to make the Conference a truly memorable experience for us all.

Franz encouraged us to remember something of our roots and produced a potted history of our endeavours for the brochure announcing this, the Fourteenth Student Conference. It seems a pity to run the risk of losing such valuable archival material so I reproduce it here, almost in its entirety. After referring to the first two very informal meetings he goes on to say:

"The 3rd (Sydney, Feb 1972) and 4th (Melbourne-Blackwood, May 1973) conferences helped to crystallize the format and preferred localities for the meetings. Namely, only students and 'recently-arrived' postdoctoral fellows present papers, in a rustic, sylvan wilderness setting. In keeping with this formula, the 5th meeting, November 1974, was held at Warrah House, the Sydney Uni's Biology Field Station, near Pretty Beach in N.S.W. Apart from the Melbourne and Sydney groups, the conferences had by this time contributors from Flinders University (Bockris' group), the Uni. of W.A. (Jim Quirk's group), R.M.I.T., Swinburne and the burgeoning ANU mob who generously undertook the job of hosting the next conference.

The 6th meeting, in May 1976, was held in the more formal surrounds of the ANU with participants from the Uni. of Queensland and a very strong input from ANU Applied Maths. It was also the inauguration of the idea of inviting a distinguished scientist to participate, and Professor Robert Street gave the opening address. It was back to the hills and forests of Blackwood in September 1977 for the 7th conference. For the 8th meeting, in November 1978, the Yarrowood Convention Centre, outside Sydney was used, and attracted, for the first time, representatives from the University of N.S.W., Bendigo CAE and SAIT. Professor Ron Ottewill was the special guest.

The ANU took responsibility for the 9th meeting (Feb. 1980) but this time held it at their field station at Kioloa on the south coast

of NSW, inviting Joe Henry from the Uni. of West Virginia and Brian Vincent as special guests.

Mt. Eliza, on Port Phillip Bay, was the site of the 10th meeting, Feb. 1982. Those who survived have a hard time remembering what happened. David Tabor of Cambridge was said to have been there.

Dick Buscall of ICI, Runcorn, was special guest for the 11th meeting at Yarrawood in May 1983; Luuk Koopal of Wageningen addressed the 12th conference, held at Roseworthy Agr. College, SA in Feb. 1985, and Dave Deamer juggled his balls for all at Kioloa, for the 13th meeting in Feb. 1987."

What more can I say, except "Thanks a lot, Franz, for a great conference!"

Bob Hunter

ACKNOWLEDGMENTS

Again we gratefully thank our supporters, the Universities of Melbourne and Sydney and the A.N.U. and the other tertiary institutions from which the delegates are drawn. Many companies have helped us by sending staff members to participate in the discussion and so to enliven the debate and add to the learning experience of the students. A few have also been prepared to make a straightforward donation towards our expenses; they were:

I.C.I. (Australia) Operations	Kodak
Albright and Wilson	AMCOR
Lever and Kitchen	and Dulux

OUR SPECIAL GUESTS

Dr. Robert O. James (Kodak Research Labs, Rochester, U.S.A.)

Prof. Pierre Bothorel (Centre de Recherche Paul Pascal, France.)

CONFERENCE PARTICIPANTS NOT PRESENTING PAPERS

Dr Jeff Aston	- ICI Research
Dr Dianne Atkinson	- Swinburne Institute of Technology
Dr Michael Baker	- South Aust. Inst. of Technology
Dr Geoff Barnes	- University of Queensland
Dr Phillipe Barois	- Australian National University
Dr Ron Beckett	- Chisholm Institute of Technology
Dr Stephen Bigger	- University of Melbourne
Dr Edward Blatt	- CSIRO Div. of Chemicals and Polymers
Dr Zoltan Blum	- Australian National University
Professor Pierre Bothorel	- Centre de Recherche Paul Pascal, France
Dr Jennifer Burnett	- Dean Hurst and Co.
Dr David Canon	- University of Sydney
Mr Celestino Carosella	- Kodak (Aust.)
Dr Vicki Chen	- University of Sydney
Dr Hugo Christenson	- Australian National University
Dr Russell Crawford	- Swinburne Institute of Technology
Dr Calum Drummond	- CSIRO Div. of Chemicals and Polymers
Dr Jiafu Fang	- Australian National University
Dr Bart Fokkink	- South Australian Inst. of Technology
Dr Daniel Fornasiero	- University of Melbourne
Dr Neil Furlong	- CSIRO Div. of Chemicals and Polymers
Dr Janine Godfrey	- Comalco
Dr Franz Grieser	- University of Melbourne
Dr Ian Harding	- Swinburne Institute of Technology
Professor Thomas Healy	- University of Melbourne
Dr Ann-Louise Holmes	- Australian Newsprint (Tasmania)
Dr Barry Hughes	- University of Melbourne
Assoc.Prof. Robert Hunter	- University of Sydney
Dr Stephen Hyde	- Australian National University
Dr Robert James	- Kodak Research Labs. (USA)
Dr Bruce Johnson	- Bendigo College of Advanced Education
Dr Marilyn Karaman	- Australian National University
Dr Yuki Kawanishi	- Australian National University
Dr Patrick Kekicheff	- Australian National University
Dr Roland Kjellander	- Australian National University
Dr Y K Leong	- University of Melbourne
Dr George Levay	- South Australian Inst. of Technology
Dr David Mackay	- Albright and Wilson (Aust.) Ltd

Dr Amanda Neil	- Australian National University (Memtec)
Professor Barry Ninham	- Australian National University
Dr Richard O'Brien	- University of New South Wales
Dr David Parris	- ICI Research
Dr Richard Pashley	- Australian National University
Dr Jian Bang Peng	- University of Queensland
Professor John Ralston	- South Australian Inst. of Technology
Dr Tim Senden	- Australian National University (Memtec)
Dr Roger Smart	- South Australian Inst. of Technology
Dr Margaret Snare	- ICI Research
Prof. Slawowir Sobieraj	- South Australian Inst. of Technology
Dr Trevor Taylor	- Kodak (Aust.)
Dr Peter Thistlethwaite	- University of Melbourne
Dr Matt Trau	- University of Melbourne
Dr Sylvia Underwood	- Dulux Australia
Dr Theo Van de Ven	- Pulp and Paper/McGill University
Dr David Waite	- ANSTO
Dr Greg Warr	- University of Sydney
Dr Len Warren	- CSIRO Division of Mineral Chemistry
Dr John Wells	- Bendigo College of Advanced Education
Professor Lee White	- University of Melbourne

FOURTEENTH AUSTRALIAN COLLOID AND
SURFACE CHEMISTRY STUDENT CONFERENCE

AUGUST 1988, ALBURY NSW

PROGRAMME

Opening Session

Monday, August 29

Lake Hume Resort, Albury

12 noon - 1.00 pm

LUNCH and Registration

1.00 pm - 3.00 pm

COLLOID I Chairman: Bob Hunter

1.00 pm

Opening Address: Franz Grieser

1.20 pm

Arthur Dimitriou, University of Sydney

"High frequency transport properties of
colloidal suspensions"

1.40 pm

Alice Lamb, University of Sydney

"Electrokinetic measurements at high
frequency of inorganic sols"

2.00 pm

Ewen Silvester, University of Melbourne

"Synthesis and properties of transparent
colloidal chalcopyrite"

2.20 pm

David Scoberg, University of Melbourne

"Reductive dissolution of colloidal
haematite"

2.40 pm

Paul Mulvaney, University of Melbourne

"Electron transfer to colloidal iron
oxide"

3.00 pm

AFTERNOON TEA

3.20 pm - 4.40 pm

SURFACTANT I Chairman: Tom Healy

3.20 pm

Greg Allan, University of Melbourne

"The composition of the aqueous and micellar
phases of multicomponent nonionic surfactant
systems"

3.40 pm

Patrick Houlihan, University of Melbourne

"A comparative study on a series of EPE
block copolymers"

- 4.00 pm Rose Amal, University of N.S.W.
 "Colloid Aggregation Kinetics -
 Investigation by Dynamic Light Scattering"
- 4.20 pm Mark Rutland, Australian National
 University
 "Adsorption of non-ionic surfactants to mica
 surfaces"
- 4.40 pm *AFTERNOON TEA*
- 5.00 pm - 6.00 pm *SURFACTANT II* Chairman: Franz Grieser
- 5.00 pm Matthew Lay, University of Melbourne
 "Acid-base indicators in water/oil emulsions"
- 5.20 pm Ian Barnes, Australian National University
 "Phase behaviour of some surfactant systems"
- 5.40 pm Ewa Radlinska, Australian National University
 "Calorimetry as a probe of microstructure"
- 6.00 pm *DINNER*
- 7.30 - 8.30 pm *COAL* Chairman: Ian Harding
- 7.30 pm Simon Hall, South Australian Institute of
 Technology
 "Surface chemistry of Victorian brown coal"
- 7.50 pm Peter Guy, Swinburne Institute of Technology
 "Surface chemistry of activated carbons"
- 8.10 pm Gregor Christie, Swinburne Institute of
 Technology
 "Role of polymers in brown coal-water
 suspensions"

Tuesday, August 30

- 9.00 - 10.40 am *MONOLAYERS* Chairman: Neil Furlong
- 9.00 am Kym Walker, University of Queensland
 "Equilibrium penetration of octadecanol
 by sodium dodecyl sulfonate"
- 9.20 am Robert Urquhart, University of Melbourne
 "Fluorescent studies of air-water monolayers"

- 9.40 am Justin Gooding, University of Melbourne
"Forster energy transfer in Langmuir-Blodgett films"
- 10.00 am Bronwyn Battersby, University of Queensland
"Monolayer and bilayer studies on phospholipids"
- 10.20 am Annette Murphy, University of Melbourne
"Energy transfer in a monolayer at the air-water interface"
- 10.40 am *MORNING TEA*
- 11.00 am - 12.20 pm *COLLOID II* Chairman: Ron Beckett
- 11.00 am Kaye Green, Bendigo College of Advanced Education
"The effect of ionic strength and anion type on adsorption of cations on kaolin"
- 11.20 am Geoff Day, Chisholm Institute of Technology
"The adsorption behaviour of some pesticides"
- 11.40 am Grant Douglas, Chisholm Institute of Technology
"The characteristics of colloidal matter in river water"
- 12.00 pm Peter Sanciuolo, Swinburne Institute of Technology
"Heavy metal removal from industrial waste by adsorbing colloid flotation"
- 12.20 pm *LUNCH*

Weather permitting, the afternoon will be devoted to sporting activities - to be arranged. If the weather is inclement, the Tuesday evening session will be conducted some time in the afternoon.
- 6.30 pm *DINNER*
- 7.30 - 9.00 pm *SPECIAL SESSION* Chairman: Lee White
- 7.30 pm Janine Kibblewhite, ICI Surface Science Laboratories
"Acid-base equilibria at the air-water interface"

- 7.45 pm Michael Johnston, ICI Surface Science
Laboratories
"Selective agglomeration of mineral fines"
- 8.00 pm Mark Griffiths, University of Melbourne
"Problems in elastohydrodynamics"
- 8.15 pm Hayden Aspinall, University of Melbourne
"Computer simulation of a porous material"

Wednesday, August 31

- 9.00 - 10.40 am COLLOID III Chairman: John Ralston
- 9.00 am David Hewitt, South Australian Institute of
Technology
"Particle sizing by photosedimentometry"
- 9.20 am Gayle Newcomb, South Australian Institute of
Technology
"Dynamic contact angles"
- 9.40 am Darren Rodda, Bendigo College of Advanced
Education
"Modelling the effect of temperature on
adsorption"
- 10.00 am Kate Wansbrough, Swinburne Institute of
Technology
"Surface modification of kaolin by polymeric
additives"
- 10.20 am William Ducker, Australian National
University
"Calcium binding to surfaces containing
carboxylic acid groups"
- 10.40 am MORNING TEA
- 11.00 am - 12.40 pm THEORY Chairman: Barry Ninham
- 11.00 am Phillip Hofflin, University of Melbourne
"Mathematical models of double layer
interaction"
- 11.20 am Andrew Fogden, University of Melbourne
"Contact angles on elastic solids"

- 11.40 am Sten Sarman, Australian National University
 "Statistical mechanical calculations of oscillatory forces between surfaces"
- 12.00 pm Christine Mangelsdorf, University of Melbourne
 "Colloidal electrokinetics"
- 12.20 pm Andrej Panjkov, University of Melbourne
 "Numerical solution of a time dependent sedimentation problem"
- 12.40 pm *LUNCH*
 The afternoon will be devoted to a tour of the Rutherglen winery district, with stops at three wineries for tasting, buying and a winery tour. Buses leave at 1.30 pm.
- 7.00 pm *CONFERENCE DINNER*

Thursday, September 1

- 9.00 - 11.00 am COLLOID IV Chairman: John Ralston
- 9.00 am Dave Diggins, South Australian Institute of Technology
 "Contact angles on particles"
- 9.20 am Stephen Grano, South Australian Institute of Technology
 "The behaviour of fine, oxidized particles in the lead/zinc concentrates at Mt Isa mines"
- 9.40 am Sean LeCount, South Australian Institute of Technology
 "Pyrite flotation in the absence of collectors"
- 10.00 am Robyn Wood, South Australian Institute of Technology
 "Characterisation and separation in mixed oxide systems"
- 10.20 am Stephen Gray, University of Melbourne
 "Heterocoagulation of magnetite and gold particles"

10.40 am Peter Weissonborn, Curtin University of
Technology
"8-hydroxyquinoline as a froth flotation
collector for Niobium and Tantalum
minerals"

11.00 am *MORNING TEA*

11.20 - 1.00 pm *SURFACTANT III* Chairman: Ric Pashley

11.20 am Irene Baker, University of Melbourne
"Formation of charge transfer complexes in
micelles"

11.40 am Mirjana Prica, University of Melbourne
"Flash photolysis in micellar solutions"

12.00 pm Cynthia Lean, Australian National University
"Studies on the Murchison meteorite"

12.20 pm Stan Miclavic, Australian National University
"Interaction between grafted poly-electrolyte
brushes"

12.40 pm Closing remarks

1.00 pm *LUNCH*

END OF CONFERENCE

ABSTRACTS

Transport Properties of Model Colloidal Suspensions

Arthur Dimitriou (University of Sydney)

The first part of this paper gives a discussion of high frequency dielectric dispersion; the second part is a discussion of the making and characterising of monodisperse, inorganic colloids.

The phenomenon of dielectric dispersion is observed when a colloidal suspension acts both as a capacitor and a conductor in an alternating electric field. The term refers to a frequency region in which the permittivity of the system changes significantly. It is measured in terms of the complex conductivity, K^* , which is related to the conductivity, σ , and the permittivity, ϵ' , of the suspension.

O'Brien (1) gives a theoretical analysis of the high frequency dielectric dispersion of a colloid which occurs at a frequency of order $\kappa^2 D$, where κ^{-1} is the thickness of the double layer and D is the ion diffusivity. He shows that K^* is directly related to the dipole strength, S , of each particle and that the surface conductivity of the particles, K_s , can be calculated from S . The total diffuse layer charge, σ_d , can then be obtained from K_s ; the electrophoretic mobility, μ_e could also be obtained as a function of frequency.

Previous studies (2) had indicated that, in latex systems, the shear plane was located some distance out from the Outer Helmholtz Plane. Further experiments are required, on different systems, to determine the extent of this phenomenon.

Problems of choosing and making a suitable inorganic colloid were outlined and a discussion given of homogeneous nucleation and particle growth. Suspensions of monodisperse cerium oxide were currently being prepared using the technique of Matijevic (3). Suspensions were characterised by determining the radius of particles, suspension density, volume fraction, and particle density, together with zeta potential and surface charge over a range of pH, using a variety of techniques.

REFERENCES

1. O'Brien, R.W. *J. Colloid Interface Sci.* 113, 81, (1986).
2. Midmore, B.R., Hunter, R.J. and O'Brien, R.W., *J. Colloid Interface*

Electrokinetic Measurements on Inorganic Sols at High (MHz) Frequency

Alice Lamb (University of Sydney).

Electroacoustic effects have recently been described as offering a new technique for the measurement of the electrokinetic properties of colloidal suspensions. The effect is based on the fact that, when a sound wave of high frequency is passed through a colloidal suspension, a measurable macroscopic potential is generated and this is defined as the Colloid Vibration Potential. This potential has been shown to be related to the electrokinetic properties of the colloid interface (1). The theory is based on an analysis for smooth monodisperse spheres with thin double layers.

The aim of the project is to experimentally verify the theory using some possible model colloids, by comparing the high frequency mobility with that obtained by conventional electrokinetic techniques such as microelectrophoresis.

REFERENCE

1. O'Brien, R.W., *J. Fluid Mech.* 190, 71 - 86 (1988).

Synthesis and Properties of Transparent Colloidal Chalcopyrite

Ewen Silvester (University of Melbourne)

Transparent colloidal chalcopyrite (CuFeS_2) has been successfully synthesised in aqueous solution. The procedure requires prior preparation of colloidal haematite¹ (Fe_2O_3 , 3 nm) and injection of this aqueous sol with cupric nitrate into a boiling solution of hydrogen sulphide. The purity of the product is sensitive to initial pH, and consequently, to total dissolved sulphide. Optimization of pH results in a solid phase of which greater than 90% by mass is chalcopyrite.

The identity of the solid phase has been determined by XRD, electron diffraction/microscopy and EDX (elemental analysis). Particle sizes are within the range 5-9 nm. Dilute sols are purple

in color and feature an absorbance maximum at 480 nm.

In the presence of air, colloidal chalcopyrite is observed to oxidize rapidly at first, then more slowly, typical of metal sulphide reactions involving the formation of a solid product layer on the outside of the mineral surface. Spectroscopic analysis of the reaction products suggests the formation of iron oxide and copper sulphide phases. This is, in part, supported by electron diffraction analysis of the solid phases formed.

Various workers, but in particular Heyes and Trahar², have established that under controlled conditions of oxidation, the surface of the mineral chalcopyrite becomes bulk hydrophobic (ie: it is recoverable by flotation without collectors) at an E_h of approximately +200 mV (s.h.e). The present synthetic colloidal chalcopyrite undergoes a significant spectral change at a similar potential. The spectral change corresponds to conversion of the $CuFeS_2$ to, in part, CuS (covellite) which even in the colloidal form shows evidence of bulk hydrophobicity.

REFERENCES

1. Sorum, C.H., J. Am. Chem. Soc. 1928 50, 1263-7.
2. Heyes, G.W. and Trahar, W.J., Int. J. Miner. Process. 1977, 4, 317-44.

Reduction of Colloidal Haematite

David Scoberg

The reduction of colloidal haematite, in alkaline solution was studied by monitoring the concentration of a reducing free radical, a zwitterionic viologen radical, using absorbance spectrophotometry. The radical was produced using standard radiolytic techniques. Steady-state photolysis experiments were used to supplement the data obtained from the steady-state radiation experiments.

It was found that although the colloidal haematite could be partially reduced to magnetite, the reduction was hindered by the hydrogen peroxide formed during irradiation. A reaction sequence, which involves the cyclic regeneration of hydrogen peroxide, was proposed to account for the observed varying rates of formation of residual free radical.

The Effect of the Zeta Potential on Electron Transfer to Colloidal Iron Oxide

Paul Mulvaney

The rate of electron transfer from methyl viologen (MV^+) and zwitterionic viologen (ZV^-) radicals to colloidal iron oxide (5 nm diameter) has been used as a probe of the oxide double layer structure. The radicals were produced by pulse radiolysis and the rate of transfer was followed spectrophotometrically at 600nm, where the radicals have extinction coefficients of $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Both the solution pH and the ionic strength had a dramatic effect upon the rate of transfer.

The results were quantitatively modelled using a Nernstian surface potential and by assuming that the plane of electron transfer coincided with the shear plane of the oxide. The rate of transfer with respect to the rate at the pzc was found to obey

$$\log k_{(pH)} = \log k_{(pzc)} - \beta(pH - pzc) - (\beta + z)\zeta F/2.3 RT,$$

where β is the anodic transfer coefficient, z is the radical charge and ζ is the zeta potential.

The dependence of the rate of transfer on the electrolyte concentration (NaClO_4) was modelled using a simple Zero Order Stern model from which a value of $400 \pm 30 \mu\text{F cm}^{-2}$ for the inner layer capacitance was found.

The composition of the Aqueous and Micellar Phases of Multicomponent Nonionic Surfactant Systems

Greg Allan (Melbourne)

The monomer concentration of penta-ethylene glycol mono-n-dodecyl ether ($C_{12}E_5$) has been measured in aqueous solution above and below the c.m.c. by ultrafiltration. The filtrate was analyzed by G.C. to determine the monomer concentration. Micellar pseudo-phase concentrations were inferred by mass balance. Results indicate that the monomer concentration above the c.m.c. increases with total concentration at a far smaller rate than below the c.m.c. Ultrafiltration membranes used thus far have been of small pore size and have shown similar monomer concentrations above the c.m.c. As

the largest of these membranes would allow an aggregate no larger than 25 monomer units to pass, there appear to be very few aggregates of 25 or fewer monomer units. This agrees well with the mean aggregation no. of 112 ± 10 determined by Herrington *et al.*¹

It is planned to extend this technique to multicomponent systems and compare the monomer concentrations measured to a phase separation-ideal mixing model of micellization developed elsewhere².

REFERENCES

1. Herrington, T.M. and Sahi, S.S., *J. Colloid Interface Sci.*, **121**, 107 (1988).
2. Clint, J.H., *J.Chem. Soc., Trans. Faraday 1*, **71**, 1327 (1975).

A comparative study on a series of EPE Block Copolymers Patrick Houlihan (Melbourne)

The block copolymer poly (ethylene oxide-propylene oxide-ethylene oxide), EPE, is composed of hydrophilic EO segments which are highly soluble in aqueous solution (ref fig. 1). Therefore by varying the number of propylene oxide $n(\text{PO})$, and ethylene oxide $n(\text{EO})$ residues, the properties of the polymers differ markedly in aqueous solution.

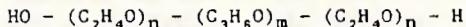


Fig. 1. Chemical structure of EPE block copolymer

It is known that EPE forms polymolecular aggregates at high concentrations. Such aggregates contain a core of relatively hydrophobic PO and are surrounded by a shell of hydrophilic EO.

The aim of this study is to investigate the effects of varying the $n(\text{PO})$ and $n(\text{EO})$ on the physiochemical properties in aqueous solution.

Using pyrene as a spectroscopic probe the UV/Vis absorbance spectrum of pyrene was recorded for each EPE polymer. The presence of an isosbestic point indicated the partitioning of pyrene between water and the hydrophobic core of the EPE aggregate. Therefore association constants, K , of pyrene to the EPE polymers were calculated. The association constants reflect the hydrophobicity, or compactness, of the aggregate.

It was found that an increase in $n(\text{PO})$ caused K to increase, while an increase in $n(\text{EO})$ caused K to decrease. This may be due to the increase in $n(\text{PO})$ causing the aggregate to fold more extensively, whereas an increase in $n(\text{EO})$ may cause the molecular interfacial area of the aggregate to increase.

The following empirical relationship relating the association constant to EPE was obtained

$$K = 100 \times n(\text{PO}) - 10 \times n(\text{EO}).$$

Absorption of Nonionic Surfactant to Mica

Mark Rutland (ANU)

Much is known of the adsorption of cationic surfactants to negatively charged surfaces like mica. The adsorption is strong due to electrostatic attraction as well as the reduction in hydrophobic surface area. However, far less is known of the adsorption of nonionic surfactants to such surfaces. If the surface is hydrated or hydrogen bonding (like a silica surface), or hydrophobic then the adsorption of nonionic surfactant can be readily understood. It is not obvious, however, whether nonionics would adsorb to a clean mica surface or even what orientation they would have were they to do so.

It is important that this system be examined, as it has implications for tertiary oil recovery (from which cationic surfactants are excluded due to their high rate of loss by adsorption to negative rock surfaces). Our initial investigations, using the surface forces apparatus, reveal that there is indeed a weak adsorption of the nonionic surfactant pentaoxyethylene mono n -dodecyl ether to mica and that it is dependent on salt concentration and is competitive with adsorbing counter ions such as sodium.

Statistical Mechanics and Small-Angle Scattering of One-Dimensional Fluids

Ian S. Barnes (ANU)

The interpretation of small-angle scattering from systems of surfactant aggregates is beset by theoretical difficulties. Noone knows how to include enough geometry in the statistical mechanics,

but on the other hand a purely geometrical approach seems at first sight to be unphysical. (The problem in the statistical mechanics is how to write down a partition function which averages over all possible aggregate shapes).

This investigation of a simple, exactly soluble one-dimensional system makes an interesting analogy with the more obscure three-dimensional problem, and provides a useful reference point for further work. The meaning of the scattering curve can easily be understood in terms of the underlying physics. Furthermore, the statistical mechanics and the geometry give identical results.

Calorimetric study of the Microstructural variation in Ternary Microemulsions

Ewa Radlinska (ANU)

The variation of the specific heat in the study of oil, water and surfactant systems should be a good indication of the conformational freedom of hydrocarbon chains as well as of the amount of bound water versus bulk water.

In this work, the specific heat of a ternary mixture of water, didodecyltrimethylammonium bromide and cyclohexane within the microemulsion phase region was measured using a Perkin-Elmer DSC-4 scanning calorimeter. The measurements were performed in the temperature interval 10-40°C and as a function of the composition.

The results of specific heat measurements are in qualitative agreement with microstructural models as well as previous experimental results of SAXS, SANS, and electrical conductivity. Thus, the calorimetric technique seems to be useful for characterization of microstructures.

The Surface Chemistry of Activated Carbons

Peter Guy (Swinburne)

The high porosity and chemical reactivity of Victorian brown coals coupled with their low inherent mineral matter contents make them excellent feedstocks for activated carbon preparation. However the lower fixed carbon content and the soft friable nature of the coals has, in the past, hindered the production of high grade attrition resistant carbons.

The use of alkalis such as ammonium hydroxide or Group I/II metal

hydroxides, as additive to brown coal, produces hard feedstocks which still retain their resistance to attrition after activation. The porosity of these feedstocks is very low due to the dissolution of the original brown coal structure during alkaline digestion, and activation is necessary to reintroduce porosity. Potassium appears unique amongst the alkali metals in its ability to generate high porosity without the need for extensive carbon burnoff.

This presentation will review the preparation of hard activated carbons from Victorian brown coal, and provide chemical and physical data comparing these carbons to those based on coconut shell for the CIP (gold recovery) process. The current understanding of the process of gold adsorption onto carbon will also be reviewed.

Energetics of Adsorption onto Surfaces

Gregor Christie (Swinburne Institute of Technology)

A thermodynamically rigorous theory and experimental technique have been developed to investigate the energetic interactions between surfaces and adsorbate molecules. The technique is sensitive at low relative vapour pressures where the Clausius Clapeyron technique can be difficult to use.

The heat of immersion of the adsorbent is determined at various points along the isotherm where the precoverage can be accurately measured gravimetrically. A relationship is derived relating the heat of immersion to the isosteric heat via an integration.

The energetics of adsorption of water onto two industrially significant surfaces (zeolite and brown coal) has been determined and the results interpreted in terms of surface mobility of adsorbate molecules.

Equilibrium Penetration of Octadecanol by Sodium Dodecyl Sulfonate Kym Walker (Queensland)

The interaction between an insoluble monolayer and a soluble surfactant (contained in the aqueous phase directly beneath the monolayer) is experimentally observed by changes in surface pressure-area isotherms of that monolayer. In the case of the system being studied, it is thought that these changes result from the

surfactant molecules entering into the spaces between the monolayer molecules, and forming a two component film. This process is known as PENETRATION.

The phenomenon of penetration is relevant to many processes in the biological and industrial fields, and it is for this reason that an understanding of the process is being pursued.

Initial work investigated the kinetics of penetration. However, lately the focus has shifted to equilibrium studies, to enable simplification of future kinetic studies.

The penetration process at equilibrium, requires that the amount of soluble surfactant contained in the film is constant, and therefore it is this quantity we wish to determine. Various thermodynamically derived theories have been developed to calculate the amount of adsorbed surfactant from the equilibrium surface pressure - area isotherms. Unfortunately, these theories do not agree completely with each other and it is therefore necessary to establish which treatment is the most appropriate to be employed. The distinction can be achieved by employing a radiolabelled surfactant which then allows the direct measurement of the amount of surfactant contained in the film from the radioactivity of the surface.

Preliminary results of the equilibrium penetration of OCTADECANOL by SODIUM DODECYL SULPHONATE indicate that two of the treatments (by (i) Hall and (ii) Pethica/Barnes, Alexander) yielded similar amounts for surfactant contained in the film. On the other hand, the third treatment by Motomura seems inadequate in some way since it was unable to be used on the results obtained from this system. The experiments employing the radiolabelled surfactant are not yet completed and will be presented at the meeting.

Forster Energy Transfer in Air-Water Monolayers

Robert Urquhart (Melbourne)

Forster energy transfer at the air-water interface between 1,1'-dioctadecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (donor) and 1,1'-dioctadecyl-3,3,3',3'-tetramethylindodicarbocyanine perchlorate (acceptor) has been demonstrated in L- β , γ -dipalmitoyl- α -lecithin (DPL) monolayers. Experiments at low ($0.03 \mu\text{m}^2 \text{s}^{-1}$) and high ($30 \mu\text{m}^2 \text{s}^{-1}$) surface diffusion of the DPL molecules

making up the bulk of the monolayer yielded the same quenching curve. The R_0 (the distance at which the rate of Forster energy transfer equals the inherent rate of deactivation of the donor molecules) for the energy transfer was calculated at about 3 nm. However, there was some scatter in the experimental points which suggested a slight degree of inhomogeneity in the monolayer.

Large inhomogeneities have been found in many other monolayer systems and so inhomogeneities seem to be important when studying monolayers. currently, fluorescence depolarisation equipment is being built to study inhomogeneities. This should shed some light on the structure of inhomogeneities in other monolayer systems.

Forster Energy Transfer in Langmuir-Blodgett Films

J. Justin Gooding (Melbourne)

The development of Langmuir-Blodgett (LB) films into useful molecular devices has been hindered by problems such as film inhomogeneities and the lack of robustness of films. An increased understanding of the physical and chemical characteristics of molecules in ordered arrays may help to solve such problems.

It is proposed to use Forster energy transfer to learn more about LB films. The experimental arrangement consists of a film containing the donor, varying numbers of films of a neutral spacer (of a known thickness) and a film of acceptors. The critical parameter is the distance where the probability of deactivation of the excited donor by Forster energy transfer and all other processes are equal. The effect on this parameter of aggregation in films will be explored.

Monolayer and Bilayer Studies on Phospholipids

Bronwyn Battersby

Phospholipid vesicles have become of considerable importance as model membranes and drug carriers for biological and therapeutical applications. A portion of the membrane surface contains the polar headgroups of the phospholipids and any small changes in the structure of the headgroups produce large changes in the behaviour of the phospholipids. Aqueous solutions undergo a phase transition with an increase in temperature and it is therefore interesting to compare the properties of the headgroup above and below this phase

transition.

Phospholipids in vesicles produce single high-resolution phosphorus-31 resonances which, by irradiation at the proton resonance frequencies, exhibit an increase in intensity upon proton decoupling. This is known as the nuclear Overhauser effect. Generally, the protons closest to the phosphorus will cause the greatest NOE.

Different NOE enhancements are observed above and below the phase transition temperature of 29°C for dimyristoylphosphatidylcholine, DMPC. At 25°C, the NOE enhancement obtained by selectively decoupling the N-methyl protons is much less than that obtained at 37°C. However, upon decoupling all the protons in the sample, the NOE enhancement at 25°C is greater than at 37°. The change in structure from lamellar sheets at 25° to multilamellar vesicles at 37° (observed by negative staining electron microscopy) therefore greatly affects the NOE enhancement.

Diffusion Studies on a Monolayer using Fluorescence Quenching Techniques

Annette Murphy (Melbourne)

Two-dimensional lateral diffusion has been studied by quenching N-(1-pyrenesulphonyl)dipalmitoyl-L- α -phosphatidyl-ethanolamine with N-n-hexadecyldimethylamine in a dioleoyl-lecithin monolayer at the air/water interface. By varying the amine concentration at a fixed compression and pyrene composition a Stern-Volmer plot was obtained. The resulting second order rate constant, k_q , was used to calculate diffusion values, D, using the Sackmann relationship, $D = k_q/4$.

Early diffusion studies in monolayers have reported values of the order of 10^{-6} cm²/sec. Recent studies have revealed values around 10^{-7} cm²/sec, more analogous to those reported for bilayers. Results for the system described above give estimated values in the range of $10^{-6} - 10^{-7}$ cm²/sec.

The Effect of Ionic Strength and Electrolyte Type on Adsorption of Cations on Kaolin

K M Green (Bendigo)

The adsorption of cations on kaolin involves two types of processes. The first adsorption process occurs at about pH 5 for all metals

studied (Cu, Cd, Co, Zn) and is dependent on the strength and type of electrolyte present. It is believed that this adsorption takes place on the negatively charged faces of the kaolin crystals and its onset is dependent on the flocculation/deflocculation of the kaolin crystals in solution.

The second adsorption process is similar in character to the adsorption that takes place on oxyhydroxide type surfaces. That is it occurs at differing pH values for different metals, it is mostly electrolyte strength and type independent and is believed to take place on the positive edges of the kaolin crystals in solution.

Suspended particulate matter (SPM) plays a vital role in the uptake and transport of nutrients, trace metals and other pollutants in natural waters. Colloidal size particles are of particular importance due to their large surface areas and hence high absorptive capacity and thus may be involved in a number of fundamental geochemical processes such as accretion, settling and dissolution. SPM, particularly in the colloidal size range also affects the optical properties of water as it is both a major absorber and scatterer of light. SPM has traditionally proved difficult to separate (fractionate) and concentrate, principally because it is a heterogeneous mixture of minerals and organic matter which may occur with a wide size range, often as dilute suspensions. A large scale preparative fractionation scheme has been developed to separate suspended particulate matter into a number of size ranges. Particular emphasis has been placed on the fractionation of colloidal sized particles which is achieved using a tangential flow filtration system. Characterisation of the fractionated SPM will involve particle size analysis and determination of mineralogy, geochemistry and optical properties.

Heavy Metal Removal by Adsorbing Colloid Flotation

Peter Sanciolo (Swinburne Institute of Technology)

The use of mixed surfactant systems in adsorptive bubble separation methods (flotation), although used extensively in the field of mineral ore flotation, is a recent innovation to the field of waste water treatment. This paper deals with research into the development of a continuous process for the treatment of electroplating wastewater. The method involves adsorption/precipitation followed by colloid flotation using a binary surfactant mixture.

The binary surfactant mixture is shown to have marked advantages over the use of one surfactant alone. The mixture is more *effective* in the removal of heavy metals (*i.e.* the percent removal is greater) and also more *efficient* (*i.e.* less total surfactant is required to reach the same results). Furthermore, the foam product from flotation using the dual surfactant mixture has improved properties

to that obtained by more conventional one-surfactant systems. When allowed to drain the foam collapses to a stable scum-like product which is easily dried (due to its high surface area).

Data is presented illustrating the success of adsorbing/precipitate colloid flotation using electroplating wastewater containing chromium (80 ppm), nickel (50 ppm) and zinc (3 ppm).

Acid-Base Equilibrium at the Air-Water Interface

Janine Kibblewhite (Melbourne)

The air-water monolayer provides a model interface that allows the controlled variation of surface charge density. Thus, monolayers can be employed to study interfacial electrostatics. The acid-base behaviour of a probe molecule located at such an interface will be different to that in bulk solution due to the reduced polarity of the interfacial microenvironment and the electrostatic surface charge of the ionizing monolayer.

Lipoidal eosin and fluorescein derivatives have been investigated in order to determine whether or not they can be used to probe the electrostatic characteristics of surfactant monolayers spread at the air/water interface. The visible absorption spectra, fluorescence emission spectra and acid-base behaviour of 5-(N-hexadecanoyl)-aminoeosin (HAE) and 5-(N-octadecanoyl)aminofluorescein (OAF) have been examined at aqueous/surfactant interfaces. For comparison the spectral properties and acid-base behaviour of closely related water soluble analogues of HAE and OAF in 1,4-dioxane/water mixture have also been studied. Lipoidal fluorescein derivatives were assessed to be the most suitable lipoidal indicators to probe the electrostatic characteristics of surfactant monolayers spread at the air/water interface. Results of a preliminary examination of the pH-dependent fluorescence properties of OAF in L- β , γ -dipalmitoyl- α -lecithin (DPL) monolayers will be presented.

Selective Agglomeration of Mineral Fines

Mike Johnson (Swinburne Institute of Technology)

Spherical agglomeration is a separation method based on particle size enlargement of suspended mineral fines. This type of separation

involves the preferential wetting of the mineral surface by oil under high shear stirring conditions.

The kinetics and selectivity of froth flotation are a function of particle size, especially below 10 μm . In this particle size regime removal kinetics decrease as does separation selectivity. Spherical agglomeration provides a complementary technique for the removal of sub 10 μm particles at low ore loadings.

The agglomeration of two sulphide minerals (100% -15 μm) from gangue was investigated at Swinburne Institute of Technology. The effect of ore loading, solids loading, oil content, mineral particle size, gangue type and oil type was correlated to the agglomerate size and grade.

Some problems in Elasto-hydrodynamics

Mark Griffiths (University of Melbourne)

The thinning of a viscous lubricant film between normally incident deformable solids is discussed. This problem is of relevance in mechanical engineering and in colloid science. Previous work in this area is reviewed. For simple geometries, numerical solution schemes and analytic approximation schemes which represent a distinct improvement over simple perturbation analyses are discussed.

Computer Simulation of Sedimentation Processes

Hayden Aspinall

The formation of a structure by the irreversible addition of sub-units from outside is a situation ideally suited to computer simulation. For example, the phenomenon of columnar microstructure in a vapour deposition onto a cold substrate is modelled by ballistic aggregation, in which particles move in straight lines and are added to a structure whenever they touch a previously added particle. Ballistic aggregation of discs onto a "seed" generates a fan structure with half an opening angle of $18.3 \pm 1.5^\circ$ (Ramanlal and Sander, 1984). They give a mean field derivation for this angle of 19.5° . An alternative derivation is given which obtains a value of 17.7° , which is closer to the observed value.

Viscous Fingering

Gerald Pereira (Melbourne)

Unstable multiphase fluid flows in porous media are of great relevance in the petroleum industry and in many industrial processes. There is a useful partial analogy between two-dimensional porous media flows and the Hele-Shaw cell. In the latter model, the effects of interfacial tension can be modelled in a physically sensible way. For two immiscible Newtonian fluids of differing viscosities in a Hele-Shaw cell, the stability of unidirectional and of radial displacements has been analysed by previous workers (Hill, Chuoke et al., Saffman and Taylor, Bataille, Wilson). This work is reviewed, and the extension of the work for a class of non-Newtonian fluids is discussed.

Particle Sizing by Photosedimentometry

David Hewitt (School of Chemical Technology)

Based on the well-established technique for photosedimentation, a new, inexpensive instrument has been developed to rapidly size particles in the range from 2 - 100 μm . The theory of photosedimentation is discussed including the application of Stokes' Law in the case of laminar flow settling as well as an extension into the region of transitional flow settling. Additional information such as surface areas and calculation of a particle shape factor is obtained from the analysis of photosedimentometry data. Comparisons are made between experimental prototypes of the new photosedimentometer and particle sizing instruments currently commercially available.

Modelling the Effect of Temperature on Adsorption

Darren Rodda

The temperature dependence of the adsorption of Cu, Zn, and Pb (each in the range 0-100ppm) onto suspensions of goethite ($\alpha\text{-FeOOH}$) in $1 \times 10^{-2} \text{M}$ KNO_3 has been studied over the range 10-70°C. The pH was held constant at 5.0 for Cu, 5.5 for Pb, and 6.5 or 7.0 for Zn.

In no case could the data be fitted by a simple Langmuir

isotherm. Results for Pb and Zn could be fitted well by a two-site Langmuir model but of the four parameters (Nm_1, b_1, Nm_2, b_2) only two (Nm_1 and b_1) could be estimated accurately.

Estimates of the enthalpy of adsorption obtained from the temperature dependence of b_1 were 16kJ/mol for Zn and 20kJ/mol for Pb.

Preliminary data for Cu shows different adsorption behaviour than that for Zn and Pb.

Surface Modification of Kaolin by Polymeric Additives

Kate Wansbrough (Swinburne Institute of Technology)

Kaolin is widely used in, for example, the ceramics, paper, polymer, paint, and rubber industries. In particular, kaolin is used as a filler for the polymer industry.

Kaolin in its unmodified form may impart required (beneficial) properties to the polymer, but simultaneously causes non-beneficial changes. Such changes are mainly due to the dissimilarity of the polymer and kaolin surface. In general, the kaolin surface tends to be fairly hydrophilic, whilst the polymer is oleophilic. Modification of the kaolin surface can render it oleophilic and thus improve compatibility between polymer and kaolin.

The relative oleophilicity is being measured by the Washburn Technique (capillary rise) and by calorimetry (heat of wetting). Both techniques are able to detect differences between modified and unmodified kaolin. The Washburn technique can only give relative values whilst Calorimetry gives an absolute value. Calorimetry values, however, only become significant on comparison between kaolin samples with different modifications. Both techniques will be investigated using a series of organic liquids containing different functional groups.

Modification of the kaolin surface has been done commercially. It is hoped a surface chemistry approach can result in the synthesis of a modifier which will improve polymer composite properties while remaining commercially viable.

Cytochrome C at the Mica Surface

William Ducker (ANU)

The surface forces apparatus of the ANU has previously been used to gain some understanding of the interaction between biological membranes by the measurement of forces between lipid bilayers. The next step towards the understanding of these membranes involves the inclusion of functional proteins to more realistically imitate those found in nature. As a first stage in this process, the adsorption to mica and interaction properties of proteins in the absence of lipid are being investigated by several workers. We have chosen to investigate Cytochrome C because its role as an electron transport protein in respiration has prompted detailed study of its structure and function.

Cytochrome C has been found to adsorb to mica directly from solution, and the interaction between Cytochrome C layers adsorbed to mica has been measured under several conditions. The mica surface is neutralized by adsorption from a dilute (10^{-7}) solution of Cytochrome C, but after the addition of salt the surface again becomes charged. The effect of exposure to a reducing agent has also been examined, and there is evidence that the surface layer is different after reduction in the bulk has occurred.

Models of the Electrical Double Layer

P. Hofflin (University of Melbourne)

An introductory view of mathematical models of the electrical double layer near charged fluid/solid interfaces.

Limits of validity of DLVO theory. Liquid state approach for primitive and civilized models and difficulties encountered for the latter due to the large dipole moments of many common polar solvents, especially water.

A scheme is presented for solving the problem of double layer interaction between two parallel plates in the Mean Spherical Approximation for a civilized model. Relevance of this theoretical model to experimental work.

A sessile liquid drop raises a ridge on the surface of the underlying solid along the three-phase line, due to the unbalanced normal component of the liquid-vapour surface tension. This effect is readily observable in experiments on suitable substrates, such as gels and thin sheets. It is widely believed that the presence of deformation invalidates the classical Young equation derived for an ideal rigid substrate. The modifications to this equation proposed in the past have taken deformation into account in an inconsistent manner. A rigorous thermodynamic treatment of the problem reveals that the true contact angle on the deformed substrate is still given by the classical Young expression, with the solid surface tensions now referred to the distorted substrate. Consequently, the force interpretation of this equation as a balance of the surface tension components tangential to the solid surface remains intact. Further, it may be shown that the angle of the liquid-vapour interface to the horizontal at the three-phase line (the so-called observed contact angle) is likewise given by this formula since the peak of the raised ridge coincides with the position of the Gibbs stress surface.

Thermodynamic and Structural Properties of Fluids in Narrow Slits

Sten Sarman (ANU)

A general method of calculating equilibrium properties of fluids in narrow slits is presented. The method is based on the exact variation of the density profile of the fluid with the slit width. The method requires accurate knowledge of the anisotropic pair correlation functions of the fluid.

In order to test the method a system consisting of a dense hard sphere fluid between hard walls has been selected. Pair correlation functions, which have been obtained using the anisotropic Percus-Yevick approximation, density profiles and solvation forces have been calculated. The results for the last two quantities agree very well with Monte Carlo simulation data. The pair correlation functions for which simulation data are not available show interesting features which never have been obtained before.

Surface conductance effects have been built into an existing model for the electrophoresis of a spherical colloidal particle moving in the presence of a weak static Electric Field (O'Brien and White, 1987).

A model of the region behind the slipping plane due to Stern and a saturating Stern layer adsorption isotherm have been assumed. The fundamental equations and boundary conditions have been modified to allow for specific interactions and movement of ions in the Stern layer.

Some sample calculations in a typical 1:1 electrolyte illustrate
(1) a large decrease in mobility, and
(2) an increase in conductivity as compared with results of the original model.

The Time-dependent Settling of Flocculated Suspensions
Andrej Panjkov (University of Melbourne)

The Buscall-White model for the settling of flocculated suspensions in batch thickening is investigated. There, the yield stress of the network must be exceeded before thickening can occur.

The highly nonlinear partial differential equations for the volume fraction of solids with a moving boundary at the top of the consolidation region must be solved numerically. The method developed converts the equations to a system of ordinary differential equations, so that they can be solved by Runge-Kutta technique, with a means to update the boundary in time. The dependence of the numerical solutions to the form of the yield stress is investigated.

Contact Angles on Particles
David Diggins (South Australian Institute of Technology)

This project deals with the measurement of contact angles in particulate systems. Static, i.e. equilibrium, capillary pressure measurements have been carried out on packed beds of angular quartz particles. The hydrophobicity of these particles is controlled by

surface methylation and esterification procedures. Measurements have been conducted as a function of particle size, degree of methylation at a given particle size and also for beds composed of mixtures of hydrophobic and hydrophilic particles. The results are interpreted in terms of the thermodynamics of wetting. Some interesting theoretical and practical issues are raised for discussion.

The Behaviour of Fine, Oxidised Particles in the Lead/Zinc Concentrates at Mt. Isa Mines

Stephen Grano (South Australian Institute of Technology)

The fundamental properties of the slime fraction of the run-of-mine ore of a lead-zinc concentrator have been studied. These have been compared to the fundamental properties of the primary grinding circuit product and used to explain differences in flotation response during standard bench scale flotation tests. Inherent difficulties in treating the slime fraction are highlighted. The slimes fraction contained sphalerite which was highly activated as a result of extensive oxidation of the galena. The rate of flotation of galena in the slimes fraction was retarded, again due to oxidation of the galena. Sphalerite activation was best countered by additions of zinc sulphate. It was also found that during combined treatment of the slimes fraction and the primary grinding circuit product, interaction effects resulted in deleterious flotation response. As a consequence, separate treatment of the slimes fraction was tested in the concentrator. This showed that improvements in lead concentrate grades were possible by this technique.

Pyrite Flotation in the Absence and Presence of Collectors

Sean LeCount (South Australia Institute of Technology)

Although the flotation of valuable mineral sulphides has been investigated extensively over a number of years, the common gangue sulphide, pyrite, has received considerably less attention. This fact, combined with the continuing problem of pyrite reducing efficiency of separations at many flotation plants, has prompted this fundamental study of the chemistry of pyrite flotation and depression.

In the current investigation, pyrite has been ground under well defined E_h conditions and then floated as a function of E_h . Experiments have been conducted in a modified Hallimond Tube, with chemical control being employed to control the E_h .

The surface species are being examined by XPS and SIMS techniques whilst UV-Vis and AA spectroscopy is being utilised in the examination of the solution phase. The mechanism of specific interactions of oxidants/reductants and collectors at the mineral-solution interface will be investigated using cyclic voltammetry, microelectrophoresis and in situ FTIR spectroscopy.

Interactions and selectivity in mineral mixture systems are being investigated in a similar manner. The significance of this work in relation to studies on real ores will also be addressed.

Characterisation, Stability and Separation in Mixed Oxide Systems

Robyn Wood (South Australian Institute of Technology)

The research involves studying the properties of ultrafine oxide particles which, in nature, constitute the components of a bauxite ore. A significant amount of the ore is present in the submicron size range which is too fine for aluminium processing. This material is presently disposed of as tailings, however research is being carried out to obtain a product which can be used as a ceramic feed.

Bauxite consists principally of gibbsite and boehmite, with the associated minerals kaolinite, quartz, hematite, goethite and anatase. The majority of the ultrafine minerals fall in the size range from 10 nm to 200 nm. Major aims of the research are to reduce the iron oxide component and to discriminate between the "iron free" minerals.

Methods have been developed for the efficient reduction of the iron content and for the partial separation of these cleaned ultrafines. The interactions between the individual mineral components of the ultrafines is now receiving attention. This is being done using pure minerals to construct artificial mixtures in order to interpret empirical results.

Individual pure minerals are being characterised by bulk chemical analysis, X-ray diffraction and surface spectroscopic analysis whilst the solid-solution interface for each mineral is probed by microelectrophoresis and potentiometric titrations to obtain pH_{iep}

and pH_{pzc} data.

This presentation focuses on the characterization of the minerals, comparison with literature studies and implications for the separation process.

Heterocoagulation of magnetite and gold particles

Stephen Gray (University of Melbourne)

Recovery of minerals from tailings requires the recovery of fine grain minerals. A heterocoagulation process known as magnetic flotation has been proposed for the recovery of such material.

To investigate this process, gold and magnetite particles are being used as a model system. The magnetite particles have been rendered hydrophobic by the addition of a silane coating.

Modelling of the system has lead to the development of energy - distance diagrams. Details of these diagrams will be discussed.

In Situ Investigation of the Tantalum Pentoxide - 8-Hydroxyquinoline Interface using Fourier Transform Infrared - Attenuated Total Reflectance (FTIR - ATR) Spectroscopy

P K Weissenborn (Curtin University of Technology, W.A.)

In the past, obtaining aqueous solution spectra using conventional infrared techniques has been difficult due to the strong absorbance of water masking weaker absorbances from other solution species. With the advent of FTIR, in conjunction with solution attenuated total reflectance (ATR) accessories, the above difficulty has been overcome, making possible the determination of aqueous solution spectra, as well as surface spectra of solids in solution.

The utilisation of FTIR spectroscopy for studying the absorption of 8-hydroxyquinoline (commonly known as oxine) onto tantalum pentoxide was aimed at obtaining a spectrum of oxine adsorbed onto the surface of tantalum pentoxide particles in aqueous solution (in situ). A Mattson FTIR spectrophotometer and Spectra-Tech cylindrical ATR accessory, known as the "CIRCLE" with a zinc selenide crystal were employed to achieve this task. The procedure involved mixing an oxine solution with tantalum pentoxide followed by centrifugal solid-liquid separation. Spectra were obtained for the supernatant (reference) and the slurry (sample) using 2000 scans each at 0.5

wavenumber resolution. Each spectrum was ratioed against that of the empty "CIRCLE" (air) before their subtraction from one another. The resultant spectrum then represented the tantalum pentoxide, its surface and any surface adsorbed oxine.

The spectrum contained a variety of bands assigned to

1. surface adsorbed water and/or hydroxy groups,
2. the tantalum pentoxide surface (Ta-O-Ta) and,
3. surface adsorbed oxine.

The most intense bands between approximately 1510 cm^{-1} and 1100 cm^{-1} were assigned to surface oxine and agreed well with the most intense bands from a spectrum of a tantalum oxinate complex prepared by previous workers. A broad, but distinct, band at 1113 cm^{-1} is assigned to the carbon-oxygen (C-O stretching frequency) group in oxine attached to the tantalum surface atoms via the oxygen atom. Other workers on metal-oxine complexes also produced a C-O stretching frequency at approximately 1100 cm^{-1} not inherent in the spectrum of oxine which has its C-O stretch at approximately 1200 cm^{-1} . No bands in the vicinity of 1200 cm^{-1} were apparent in the tantalum pentoxide-surface oxine spectrum and only a very weak band close to 1200 cm^{-1} in the tantalum oxinate spectrum was apparent. The participation of the oxine's nitrogen atom in bonding to a surface tantalum atom was difficult to determine. However, its close proximity to the tantalum atom to which the oxygen is bonded and its capacity to donate bonding electrons suggest oxine surface chelation is probable.

The above work has contributed to the evaluation of oxine as a tantalite (a tantalum/niobium mineral) selective froth flotation collector. Work is continuing on the niobium pentoxide - oxine and tantalite - oxine interfaces using the above procedure which may assist in the application of oxine or similar chelating agents to the processing of hardrock tantalite ores by froth flotation in the South West of Western Australia.

Charge Transfer Complexes in Micelles

Irene J. A. Baker (University of Melbourne)

Association constants for the ground state electron-donor-acceptor complexes formed by pyrene or 9-methylanthracene (donors) with N,N'-dimethyl-4,4'-bipyridinium dichloride (acceptor) have been

determined by absorption spectroscopy in bulk methanol, in sodium dodecyl sulphate (SDS) micellar solution and in SDS/pentanol/dodecane microemulsion.

The association constants in the latter systems were corrected to allow for the effective concentrations of acceptor and donor in the micellar/oil phase to which they are confined. Comparison of these corrected association constants with bulk association constants shows that there is an enhancement of complex formation in the micellar system and some restriction of complex formation in the microemulsion.

Considering that the positively charged acceptor is bound at the surface of the negatively charged SDS assemblies these results imply that pyrene and 9-methylantracene are preferentially solubilised in the surface region of micelles, while for the microemulsion droplets solubilisation in the oil interior is more favourable.

This method of investigating solubilisation sites of small probe molecules in self assembly systems requires that the complex formation is not affected by environment, and that there are no interfering interactions of the probes with other species in the system. Investigations in nonionic and cationic systems may be possible using the more hydrophobic acceptor N-dodecyl- N'-methyl-4,4'-bipyridinium dichloride.

Electron Transfer Reactions in Micellar Systems

Mirjana Prica (University of Melbourne)

Electron transfer reactions play important roles in biological processes such as respiration and photosynthesis. Electrical charge is transferred across membranes from one medium to another. These light-induced electron transport processes are important in the understanding of solar energy conversion.

The electron transfer between methyl viologen (MV^+) and the radical anion of benzophenone (BZP^-) has been studied in micellar solutions using the technique of flash photolysis. The electron transfer rate constant is related to the surface potential of the micelle. Results carried out on homogeneous solutions containing MV^+ and benzophenone (BZP) show that the rate constant for the electron transfer process increases as the dielectric constant of the medium increases. A water-soluble derivative of BZP,

benzophenone-4-sulfonate (BZPS), is used in media of higher dielectric constant as BZP is not soluble under these conditions. Characterisation of the BZPS transient species shows it to have an extinction coefficient of $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (measured at the absorption maximum of 630 nm) and a pK_a of 11.78. Preliminary results suggest that the rate of electron transfer is slower in the presence of a micelle.

The Role of Additives in Victorian Brown Coal - Water Slurries

Philip Tudor (Swinburne Institute of Technology)

The low cost and large reserves of brown coal, their low nitrogen and sulphur levels and the ease of transportation via pipelines all point to brown coal slurries as a viable alternative to heavy fuel oil. Coal has a lower energy yield compared to fuel oil, hence a maximum concentration is required in the slurry. High concentration slurries have been prepared, however, the key to the success of brown coal lies in further increasing the solids content in a slurry while retaining acceptable rheology (eg. minimum viscosity and prevention of "hard-cake" formation during storage).

The effects on brown coal slurries of various additives (surfactants and polymers) are being assessed by the following techniques:

1. Brookfield viscometry
2. Vane Method (for yield stress)
3. Static Settling Test
4. Redispersion Test
5. Compression Test

Brookfield viscometry gives an approximation of the slurry's viscosity and hence the effectiveness of an additive as a dispersant. The other techniques quantify the stabilizing action of additives. These results will be combined with information on coal surface structure and the orientation and coverage of the additives on the surface to obtain a complete picture of brown coal slurries in the presence of additives.

Colloid Aggregation Kinetics - Investigation by Dynamic Light Scattering

Rose Amal (University of N.S.W.)

The purpose of this study was to compare the aggregation kinetics of haematite by Dynamic Light Scattering (DLS) with the Smoluchowski model. The stability ratio and, hence, the retarded rate constant of the aggregates, was obtained theoretically using the Fuchs equations. The resulting rate constant was then fitted into the Smoluchowski model with a constant packing factor assumed to get the aggregate size.

The trend of the aggregate size curves from DLS with different salt concentration fits the model well at the beginning of the aggregation process or low salt concentration. At later times, the aggregation process detected by DLS was much faster than the one described in the model; this was probably due to the assumption of a constant packing factor.