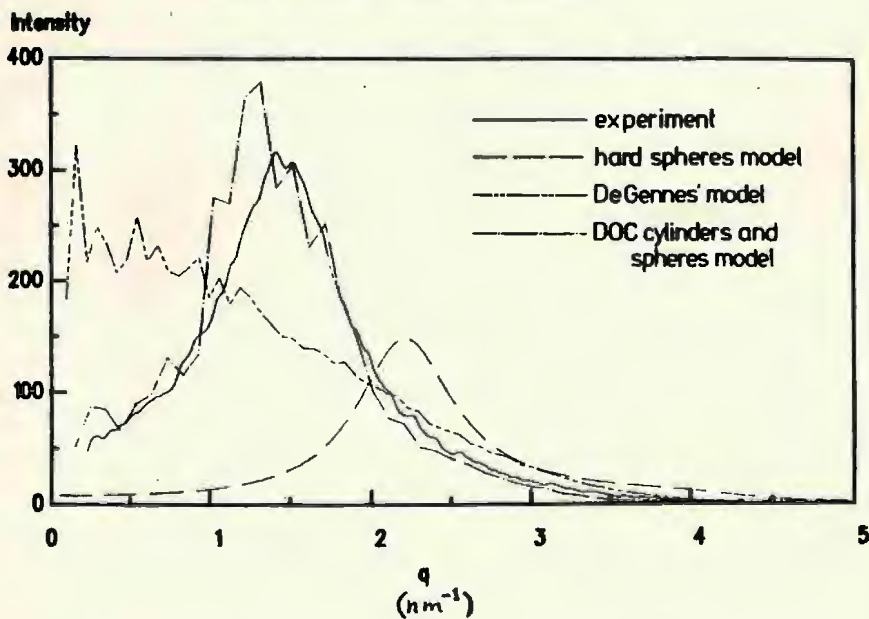


PROCEEDINGS AND ABSTRACTS
OF THE
THIRTEENTH AUSTRALIAN COLLOID
AND
SURFACE CHEMISTRY

STUDENT CONFERENCE

KIOLOA, NSW, 1987

DDAB/water/cyclohexane microemulsion



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VENUE:

THE EDITH AND JOY LONDON FOUNDATION

AT

KIOLOA, NSW

FEBRUARY 1987

A SPECIAL NOTE

The Edith and Joy London Foundation was set up as a biological field station after a gift was made to the Australian National University by Miss Joy London in 1975. The property is 5 km south of Bawley Point and approximately 46 km north of Bateman's Bay, N.S.W.

ACKNOWLEDGEMENTS

Students and University staff, C.S.I.R.O. and industry participants contributed financially to the running of the Conference, but substantial financial assistance was also provided by the University of Melbourne and the ANU. Generous support is also gratefully acknowledged from the following companies:

BHP, Tioxide (Australia), Dulux Australia, ICI Operations, Slurry systems, Catoleum Pty Ltd., Australian Dispensers, Albright and Wilson, Amcor, Australian Carbon Black, Comalco and Monsanto.

Our special thanks also go to Norma Chen and her helpers for the magnificent job they did in catering for us and, of course, to Dr Ric Pashley who organised the whole show and made it all happen.

LIST OF PARTICIPANTS NOT INCLUDED IN THE PROGRAMME:

Dr R.G. Horn, Department of Applied Maths, ANU.

Dr H.K. Christenson, Department of Applied Maths, ANU.

Ms M. Karaman, Department of Applied Maths, ANU.

A/Prof. R.J. Hunter, School of Chemistry, Sydney University.

Dr R. O'Brien, School of Maths, University of New South Wales.

Dr D.Y.C. Chan, Dept of Mathematics, University of Melbourne.

Professor Dave Deamer, Department of Chemistry, ANU.

Ms Cynthia Lean, Department of Chemistry, ANU.

Dr L.R. Fisher, Division of Food Research, CSIRO, Sydney.

Ms Emma Mitchell, Division of Food Research, CSIRO, Sydney.

Dr Ian Harding, Swinbourne Institute of Technology, Melbourne.

Dr D. Mainwaring, Swinbourne Inst. of Technology, Melbourne.

Mr Mark Cadzow, Swinbourne Institute of Technology, Melbourne.

Dr Kelvin Koys, SAIT, Adelaide.

Dr Robin Wood, SAJD, Adelaide.

Dr B.A. Pailthorpe, School of Physics, University of Sydney.

Mr P. Strasser, Albright & Wilson (Australia) Limited, Vic.

Dr S. Lenon, Dulux Australia, Victoria.

Mr R. Fish, AMCOR Research & Technology, Victoria.

Note

Information on the Australian Colloid and Surface Chemistry Student Conferences
can be obtained from:

Prof. T.W.Healy
Dept. of Physical Chemistry
University of Melbourne
Parkville, Vic 3052

or

Assoc. Prof. R.J.Hunter
School Of Chemistry
University of Sydney
N.S.W. 2006

CONFERENCE PROGRAMME

All talks were of 15 minutes duration with 5 minutes for discussion.

TUESDAY 3RD FEBRUARY

11.00 am - 2.00 pm: Arrive at the Edith and Joy London Foundation at Kioloa (see map). Sandwiches will be available.

2.00 pm Opening Session. Chairman: Professor B.W. Ninham.

2.00 pm Opening Address: Professor B.W. Ninham.

2.20 pm **Ian Barnes**, Department of Applied Mathematics, ANU.
"Calculation of small angle scattering for model microemulsion structures".

2.40 pm **Phil Attard**, Department of Applied Mathematics, ANU.
"Interactions between electroneutral surfaces containing mobile charges".

3.00 pm **Stan Miklavic**, Department of Applied Mathematics, ANU. "A theoretical study of cell surfaces with assistance from Monte Carlo calculations of surface attached polyelectrolytes".

3.20 pm

AFTERNOON TEA

3.40 pm Chairman: Dr F. Grieser.

4.00 pm **Lyn Denison (Post-doc.)**, Department of Physical Chemistry, Melbourne University. "Photophysics of water soluble copolymers".

4.20 pm **Paul Mulvaney**, Department of Physical Chemistry, University of Melbourne. "Free radical reactions with metal oxides".

- 4.40 pm **Matthew Lay**, Department of Physical Chemistry, University of Melbourne. "Spectroscopic studies of ionisation reactions at aqueous interfaces".
- 5.00 pm **Daniel Fornasiero (Post-doc.)**, Department of Physical Chemistry, University of Melbourne. "Proton n.m.r. study of the solubilisation of probe molecules into micelles".
- 5.20 pm **David Everett**, Department of Physical Chemistry, University of Sydney. "The elastic (rigidity) modulus of coagulated colloidal systems".
- 5.40 pm **A. Fodgen**, Department of Mathematics, University of Melbourne. "Contact elasticity in the presence of capillary condensation".

WEDNESDAY 4TH FEBRUARY

- 9.00 am **Chairman: Dr N. Furlong.**
- 9.00 am **Edward Blatt**, CSIRO, Division of Applied Organic Chemistry, Melbourne. "The adsorption (or non-adsorption) of molecules and ions onto semi-conductor surfaces".
- 9.20 am **Sean O'Shea**, School of Physics, University of Sydney. "Gas adsorption phenomena in solar collector tubes".
- 9.40 am **Janine Godfrey**, Department of Physical Chemistry, University of Melbourne. "The ionization behaviour of some Langmuir-Blodgett cast films".
- 10.00 am **MORNING TEA**
- 10.20 am **Peter Scales**, Department of Physical Chemistry, University of Melbourne. "Streaming potential studies on Langmuir-Blodgett films".
- 10.40 am **Mark Rutland**, Department of Chemistry, ANU. "Charging of Silica in solutions of symmetrical quaternary ammonium bromides".

- 11.00 am Jeff Aston, "Adsorption of Polydisperse nonionic surfactants at the Solid/Aqueous interface".
- 11.20 am Graeme Sutton, Department of Physical Chemistry, University of Melbourne. "Electrophoresis of spheroidal particles"
- 11.40 noon LUNCH
- 2.00 pm - 4.00 pm Free activities
- 4.00 pm Chairman: Professor T.W. Healy.
- 4.00 pm David Dunstan, Department of Physical Chemistry, University of Melbourne. "Conductivity and dielectric response of colloidal dispersions".
- 4.20 pm Simon Davies (Post-doc.), Department of Physical Chemistry, University of Melbourne. "Reductive dissolution of haematite in the presence of ascorbate".
- 4.40 pm David Hayes, Department of Physical Chemistry, University of Melbourne. "Aggregation of colloidal silver".
- 5.00 pm Ewen Silvester, Department of Physical Chemistry, University of Melbourne. "Synthesis of colloidal chalcopyrite".
- 5.20 pm Gregor Christie, Swinbourne Institute of Technology. "Surface energetics of Victorian brown coal".
- 5.40 pm David Diggins, Department of Physical Chemistry, University of Sydney. "High frequency dielectric disperion of colloids."
- 6.30 pm DINNER

THURSDAY 5TH FEBRUARY

- 9.00 am Chairman: Professor L.R. White
- 9.00 am Calum Drummond, Department of Physical Chemistry, University of Melbourne. "Solvatochromic acid-base indicators as probes of

the interfacial microenvironment of micelles".

9.20 am Peter Triandos, Department of Physical Chemistry, University of Melbourne. "Applications of fluorescent probes for studying monolayers at the air-water interface".

9.40 am Greg Allan, Department of Physical Chemistry, University of Melbourne. "Ultrafiltration of multi-component non-ionic surfactant solutions".

10.00 am Kym Walker, Department of Chemistry, Queensland University. "Purity and purification of single component surfactant solutions below the c.m.c."

10.20 am MORNING TEA

10.40 am Robert Urquhart, Department of Physical Chemistry, University of Melbourne. "Measurement of the microenvironment at the air-water interface".

11.00 am Michelle Gee, Department of Physical Chemistry, University of Melbourne. "Investigation of equilibrium wetting films".

11.20 am Gayle Newcombe, SAIT. "Thin films and movement of the three phase line of contact".

12.00 noon LUNCH.

2.00 pm - 6.00 pm Afternoon of competitive sport activity - to be arranged.

7.00 pm CONFERENCE DINNER.

FRIDAY 6TH FEBRUARY

9.00 am Chairman: Dr R.M. Pashley

9.00 am Patty McGuiggan, Department of Chemistry, ANU. "Direct measurement of forces in surfactant and NaCl solutions".

- 9.20 am Ewa Radlinska, Department of Applied Maths, ANU.
"Light-scattering studies on vesicles in
didodecyldimethylammonium hydroxide".
- 9.40 am John Parker, Department of Applied Maths, ANU. "Forces
between lipid bilayers".
- 10.00 am Geoff Francis, CSIRO, Division of Food Research, Sydney.
"Cell adhesion".
- 10.20 am MORNING TEA
- 10.40 am George Levay, SAIT. "Oil flotation of fine sulphide mineral
particles".
- 11.00 am William Ducker, Department of Chemistry, ANU. "The flotation
of quartz by double-chained quaternary ammonium ion
surfactants".
- 11.20 am Russell Crawford, Swinbourne Institute of Technology. "Flotation
models".
- 11.40 am Prof. B.W. Ninham - summing up.

END OF CONFERENCE

ABSTRACTS

CALCULATION OF SMALL-ANGLE SCATTERING FROM MODEL STRUCTURES OF MICROEMULSIONS

Ian Barnes,
Department of Applied Mathematics,
Australian National University.

The Holy Grail in the study of oil/water/surfactant systems is the ability to predict the properties and behaviour of a sample from its composition. Essential to this is the determination of microstructure, from which many macroscopic properties follow.

The only detailed information about microstructure (on a scale of a few to a few hundred Angströms) comes from small-angle scattering of x-rays and neutrons. A major problem has been the lack of a general method for predicting the scattering from arbitrary structural models. I have developed such a method, in which model structures are sampled on a cubic lattice, and assumed to have constant scattering length density in each small cubic region of the lattice. The scattering from this digitized structure is then calculated by three-dimensional numerical Fourier transformation, squaring and averaging over directions in Fourier space.

We have used this new technique in our study of the oil-rich microemulsion which exists over a large range of composition in the DDAB/water/cyclohexane system. Consideration of the counterintuitive decrease in conductivity observed as water is added has led us to discard the existing models and propose a new model for microemulsion structure: the Disordered Open Connected (DOC) model. This is based on a random network of water-filled cylinders with spheres at the points of intersection. As water is added, the coordination of the network decreases with a percolation to isolated spheres giving the observed conductivity variation. We hope to refine the model by replacing the spheres and cylinders with a surface of constant mean curvature.

Comparison of the experimental and calculated scattering curves for a particular sample at low water content confirms our rejection of the DeGennes and hard spheres models. The calculated curve for the DOC model agrees well with the experiment.

INTERACTION BETWEEN ELECTRONEUTRAL SURFACES CONTAINING MOBILE CHARGES

Phil Attard

Applied Mathematics, A.N.U.

We develop a mean field perturbation theory to describe systems with long range interactions. Here the dominant contribution to integrals involving many-particle correlation functions comes from a superposition of products of pair correlations. We use this fact to calculate the change in free energy due to turning on the tail of the potential, and also the pair correlation function, in terms of a system which interacts with short range potentials.

This method is used to describe the interaction between two, two-dimensional two component plasmas. This is proposed as a model of mica surfaces coated with mixtures of cationic or anionic surfactants, and also of charge adsorption, provided there is a degree of mobility on the interacting surfaces. The pressure results from correlations between charges on each surface.

The pair correlation function of an isolated single surface universally decays as a cubic parallel to the surface. Consequently the attractive pressure is also universal in the asymptotic limit of large separation. It is independent of the valency, surface charge density or hard core radius and goes as a cubic in separation. The effective Hamaker constant, 3.7×10^{-21} J, is comparable to that typical of van der Waals interactions of hydrocarbon across water. Electrostatic images decrease the attraction at larger separations. A particular form of the mean field perturbation theory yields the Debye-Hückel result, valid for low surface densities, and this is always a lower bound for the actual pressure of the system. Comparisons with accurate HNC calculations show that the method is valid down to separations of the order of Angstroms.

A THEORETICAL STUDY OF CELL SURFACES WITH ASSISTANCE FROM MONTE CARLO CALCULATIONS OF SURFACE ATTACHED POLYELECTROLYTES

Stan Miklovic

A thin layer of glycolipids and glycoproteins that covers most biological cells is thought to play the dominant role in reactions associated with cell-cell interactions such as occur in the immune response and in agglutination.

A theoretical study is needed for the physical nature of this layer and its response to changes in a cell's environment before an understanding of complex biological functions may be presumed.

A large- κa model is presented for a cell with a surface bound layer of polyelectrolyte molecules: a chain of negatively charged groups. The calculations involve a single-chain self-avoiding random walk ensemble in collaboration with a mean-field electrostatic theory, (described by the Poisson-Boltzmann equation).

Some of the more important results that these calculations produce include graphs of typical number/charge density profiles for the groups of the chain as a function of the distance from the surface and the response of this density to variations in the bulk conditions, in particular to variations in salt concentrations. In addition, the value of the thickness of this layer as a function of salt content is also given. This latter result proves to be of extreme importance to the situation encountered in electrophoretic studies of biological systems where it has been shown that nonuniformities in surface structure produce significantly different results in comparison to the classical Smoluchowski theory of a smooth colloid.

PHOTOPHYSICS OF WATER SOLUBLE COPOLYMERS

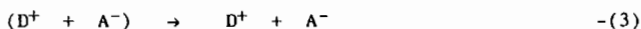
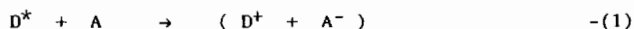
Lyn Denison

University of Melbourne.

In recent years much effort has been devoted to the study of reactions in microheterogeneous media. Among these reactions, energy transfer and electron transfer processes have been particularly emphasized, principally because of their relation to the conversion and storage of solar energy.

Contemporary efforts to directly convert solar radiation to chemical energy storage has affected many different fields of photochemistry and photophysics and has been largely responsible for the development of several new fields of research (e.g. photophysics of semiconductor colloids).

One of the fundamental problems in this field has been the separation of ion-pairs produced by excited state electron transfer i.e.,



The products D^+ and A^- are highly energetic and could serve as intermediates in a chemical chain to produce useful fuel. In homogeneous solution the overwhelming tendency is for the back reaction (eqn. 2) to be favoured over separation of the geminate pair (eqn. 3). In order to encourage eqn. 3, much effort has been expended in designing microheterogeneous

environments of various sorts, such as micelles, liposomes, bilayer membranes etc., since it is well known that in naturally occurring photosynthetic systems, the biomembrane plays a central role.

In artificial systems it is not clear that a membrane *per se* is required, and it has been proposed that functionalized polyelectrolytes may be used.

The primary goal of this research was to design polymer systems that provide for efficient charge separation upon redox quenching of a polymer-bound chromophore and to study the photophysics of the pendant chromophores. Results of redox quenching and photoionization studies will be presented.

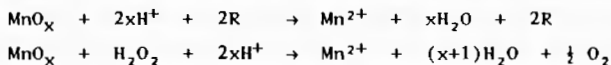
FREE RADICAL REACTIONS WITH COLLOIDAL METAL OXIDES

P. Mulvaney

Department of Physical Chemistry, University of Melbourne,

The crystal structure of metal oxides is known to play an important role in the reactivity of the oxide to various redox processes in solution. Studies of the role of the crystal structure have, however been complicated by the effects of reactant adsorption, surface area, hydration, lattice impurities or because of the inadequate control of solution conditions.

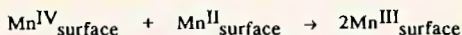
In this study we have investigated the dissolution of several colloidal manganese oxides of different crystal structure, using the isopropyl alcohol radical and a methylviologen derivative (ZMY) as reducing agents. γ -irradiation of colloidal MnO_x (α, β, γ and a new form with a crystal structure similar to pseudo rutile) in the presence of acetone/isopropyl alcohol or isopropyl alcohol (ZMV) produces Mn^{2+} at pH=3 with θ values in the range of 3.7 to 5.4, which is consistent with the mechanism:



The work to date has shown that the crystal composition of the oxides of manganese can be readily identified from the θ values of Mn^{2+} produced.

We have also investigated the kinetics of dissolution using pulse radiolysis coupled with a transient conductivity detector. The results from this work show that 3 time domains are involved in the proton up-take leading to Mn^{2+} release from the colloid, ranging from 10 μ sec to 100 sec. The temporal characteristics for the dissolution process is virtually the same for all crystal structures examined. The influence of Mn^{2+} on rate of proton up-take in the

short time domain $< 100 \mu\text{sec}$, is crucial. The more Mn^{2+} present in the sample the faster the initial proton consumption. We believe this to be due to the formation of Mn^{3+} centres on the surface due to the step.



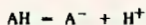
This reaction is known for higher pH systems, but not previously identified at $\text{pH} = 3$. More details of the kinetic results will be presented at the conference.

SPECTROSCOPIC STUDIES OF IONIZATION REACTIONS AT AQUEOUS INTERFACES

Matthew Lay,

Department of Physical Chemistry, Melbourne University.

A question of considerable interest and importance in Surface Chemistry is the nature of interfacial water: it is clear that the properties of interfacial water play a large part in determining the behaviour of many surfaces. We are particularly interested in the role this water plays in controlling the extent of the simple surface charging reaction:



Undoubtedly, the dynamics of proton hydration by interfacial water contribute substantially to the control of this reaction.

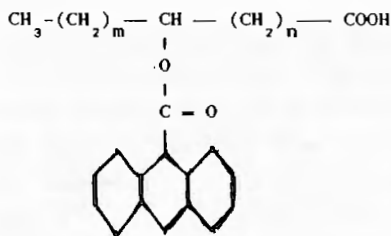
In an attempt to gain some insight into this fundamental problem, we have undertaken some novel kinetic experiments (traditionally only equilibrium measurements have been made). Our most useful tools have proved to be fluorescent probe molecules which undergo excited state ionisation. These experiments, performed on surfactant aggregates, have yielded many fascinating results. In this paper some of these results will be presented and their significance discussed.

PROTON NMR STUDY OF THE SOLUBILIZATION OF PROBE MOLECULES INTO MICELLES

Daniel Fornasiero

Department of Physical Chemistry, University of Melbourne,

There have been many investigations of the physico-chemical properties (e.g. micro-polarity, viscosity) of micelles, microemulsions and vesicles which have been based on monitoring the spectral characteristics of environment sensitive probe molecules solubilized by the host self-aggregate^{1,2}. Among the various spectroscopic techniques used, fluorescence measurements, and in particular fluorescence quenching, have been very popular³. Interpretations of these measurements are dependent on the exact location of the probes in the micelle: in the micelle core or in the head group region. Recently some "depth" probe molecules have been used to resolve this problem. They consist of a fluorescent probe attached at different positions along an alkyl chain.



Good correlations have been reported between fluorescence quenching measurements and the position of the fluorescent probe along the solubilized alkyl chain⁴. To verify the merits of this method, we have carried out a proton NMR study of various micelles and monitored the difference in chemical shift and bandwidth of the proton resonance peaks as a function of the concentration of the probe added and the position of the fluorescent moiety along the chain.

References:

1. K.N. Ganesh, P. Mitra and D. Balasubramania, *J.Phys.Chem.*, **86**,4291(1982).
2. M. Almgren, F. Grieser and J.K. Thomas, *J.An.Chem.Soc.*, **102**,3188(1980).
3. F. Blatt and W.H. Sawyer, *Biochem, Biophys. Acta*, **822**,43(1985).
4. S.R. Johns, R.I. Willing, K.R. Thulborn and W.H. Sawyer, *Chem.Phys.Lipids*, **24**,11(1979).

THE ELASTIC (RIGIDITY) MODULUS OF COAGULATED COLLOIDAL SYSTEMS

D.W. Everett

Department of Physical Chemistry, The University of Sydney. 2006

Rheological measurements of the viscous and elastic properties of coagulated model colloids were undertaken to investigate the region of close interparticle interactions (< 5 nm). Spherical, monodisperse polymethyl-methacrylate and polystyrene colloids were coagulated by the adsorption of cationic CTAB surfactant onto the particle surface, and the consequent ζ -potential measured by microelectrophoresis.

Models have been proposed to describe the colloidal characteristics (particle radius, volume fraction and ζ -potential) in terms of the viscous dissipative parameters measured in a rotating outer cylinder Couette viscometer¹. These models have now been extended² to describe the non-dissipative elastic behaviour in terms of the colloidal characteristics using parameters derived from the viscous data.

All elastic measurements were made on a Rank Bros. pulse shearometer which has the advantage over constant stress rheometers of being able to measure the elastic shear modulus, G , without disrupting the delicate network structure of flocs in the coagulated sample. The pulse shearometer measures the velocity, u , of a transverse wave pulse through a sample where the amplitude of the wave is 8×10^{-5} radians. This is subsequently related to the shear modulus by the relationship $G = \rho u^2$, where ρ is the density of the sample.

The shear modulus has been predicted using only one fitting parameter, d , which is the interparticle separation at the minimum potential. Elastic data has been fitted using $d \approx 0.5$ nm which agrees well with estimates for d , from viscous data.

Elastic measurements have also been made on Na^+ -Kaolinite samples as a function of pH and ionic strength. Due to the anisometric nature of kaolinite, the particles can orientate in several directions as coagulation occurs, and this is detected by the pulse shearometer.

References:

1. Firth, B.A. and Hunter, R.J. *J. Colloid and Interface. Science* 57,266,(1976).
2. van de Ven, T.G.M. and Hunter, R.J. *J. Colloid and Interface. Science* 68,135,(1979).

CONTACT ELASTICITY IN THE PRESENCE OF CAPILLARY CONDENSATION

A. Fogden

Dept of Applied Mathematics, University of Melbourne.

If two elastic bodies are in contact in an atmosphere of undersaturated vapour of a wetting liquid then the vapour can exist in equilibrium with a ring of liquid around the contact circle. The purpose of this talk is to outline a generalisation of the existing non-adhesive and adhesive theories of contact elasticity, developed by Hertz and Johnson, Kendall and Roberts (JKR) respectively, in which this effect, referred to as capillary condensation, is taken into account.

The introduction of such a tensile normal stress on part of the surfaces outside the contact region can be handled conveniently using Hughes' physically consistent theory. This enables both generalised problems to be formulated as a system of three equations in four unknown parameters, from which the load-contact radius curves for each theory can be generated numerically in a simple manner.

Significant insight into the problem can be gained however, by also proceeding analytically by approximations based on assumptions as to the size of the fundamental dimensionless parameter k in both theories. If k is sufficiently small then in the generalised Hertz theory the capillary condensation introduces adhesion in precisely the form of the original JKR theory, where now the solid-vacuum surface energy has been replaced by the liquid-vapour surface energy. Further, in the generalised JKR theory we observe a simple switch between the liquid-vapour and solid-vapour original JKR forms when the adhesion due to the one dominates the contribution of the other.

THE ADSORPTION (OR NON-ADSORPTION) OF MOLECULES AND IONS ONTO SEMI-CONDUCTOR SURFACES

Eddie Blatt

CSIRO Division of Applied Organic Chemistry.

The adsorption of pyrene, 1-pyrenesulfonate (SPS) and I^- from aqueous solution at pH 3 onto TiO_2 particles is examined by fluorescence probe, centrifugation and electrophoresis techniques. At low probe concentrations, neither pyrene nor SPS molecules adsorb onto TiO_2 particles of 9 nm diameter. Adsorption of pyrene was observed when larger TiO_2 particles were used, and for SPS onto the 9 nm diameter particles by increasing the initial concentration of

probe. Electrophoretic mobility measurements of TiO_2 dispersed in aqueous 10^{-2} M I^- show that specific adsorption of I^- onto a positive TiO_2 surface does not occur.

GAS ADSORPTION PHENOMENA IN SOLAR COLLECTOR TUBES

Sean O'Shea

School of Physics, Sydney University.

Evacuated tubular solar collectors consist of two concentric glass cylinders sealed at both ends, the volume between the cylinders being under vacuum. The inner tube is coated with a graded stainless steel to a C:H surface with a copper underlayer. This surface absorbs the incident solar energy and has a low infra-red emittance. Such tubes can reach temperatures of 300°C under no load conditions. For reasons of cost and safety it is required to limit this maximum temperature to near 100°C . The method being pursued is the introduction of an adsorbable gas (eg. benzene) into the tube. At low temperatures most of the gas remains absorbed onto the inner tube surface and the tube operates as normal. As the temperature rises gas desorbs and the vacuum is degraded. The extra conduction heat loss mechanism will reduce the maximum tube temperature.

Adsorption isotherms for benzene and nitrogen were found experimentally and the isosteric heats calculated. Baking the tube at 500°C for 1 hour was found to

- i) increase the adsorption area from $\sim 1 \times$ the geometric surface area to $\sim 50 \times$ the geometric area,
- ii) increase the affinity of the benzene for the surface from ~ 17 kJ/mol to ~ 60 kJ/mol.

Comparison of the nitrogen and benzene results showed that the system exhibits strong physisorption. These results are consistent with spectroscopic data. The physical model used to describe the results is that an unbaked surface consists of two solid cores, one being a collection of small aromatic structures, the other being groups of saturated hydrocarbons. On baking, hydrogen is evolved, the aromatic structures increase in size (~ 100 fold) and the surface develops large pores. Further intense baking will collapse the surface due to compaction.

THE IONIZATION BEHAVIOUR OF SOME LANGMUIR-BLODGETT CAST FILMS

Janine S. Godfrey

University of Melbourne.

Uniform, well defined surfaces do not abound in nature. One way that we can overcome this difficulty is to build the surfaces ourselves, incorporating in them the characteristics necessary to obtain the desired information. The surfaces we have made are Langmuir-Blodgett cast films. Using these we aim to obtain the charge and potential of the surface as a function of electrolyte concentration and pH in order to compare existing theories of the double layer with experimental results and hopefully to modify these theories to satisfactorily explain the complex way in which charge develops at an interface.

The cast films contain an ionizable chromophore in a supporting lipid matrix. We have chosen some well studied acid-base indicators and dielectric sensitive compounds as the ionizable chromophores so that the degree of ionization of the surface and an indication of the interfacial dielectric environment can both be obtained by means of our ATR (Attenuated Total Reflectance) technique.

The technique gives excellent sensitivity and reproducibility and our studies have highlighted some interesting phenomena at the onset of charge development at the interface. These effects will be discussed in terms of several models.

STREAMING POTENTIAL STUDIES ON LANGMUIR-BLODGETT FILMS

P.J. Scales

Department of Physical Chemistry, The University of Melbourne,

The measurement of a streaming potential can provide information as to the zeta potential and the charge density at or about the hydrodynamic plane of shear of a charged interface. An apparatus has been developed to measure the streaming potential on flat rectangular plates. A simple rectangular capillary is formed between two plates and liquid is flowed in both directions and the streaming potential measured. Langmuir-Blodgett coating of charged monolayers onto the plates where the charge density of the coating is predetermined by the characteristics of the cast film allows the development of a model ionic surface.

Results of measurements on monolayers on fused silica of a negative probe molecule (4-heptadecyl-7-hydroxycoumarin) embedded in a neutral polymer

(poly- (vinyloctadecyl ether)) at a predetermined charge density show the charge on the underlying silica surface to be unsuppressed by the addition of the monolayer film and of over-riding influence on the measured potential. The complete suppression of the underlying charge with readily available positively charged molecules through adsorption or Langmuir-Blodgett coating was found to be difficult due to the high surface site density of the silica. No such problems were experienced with other base surfaces such as muscovite mica as the surface site density was considerably lower.

Results of streaming potential experiments of films adsorbed and coated onto silica and mica substrates will be presented.

CHARGING OF SILICA IN SOLUTIONS OF SYMMETRICAL QUATERNARY AMMONIUM BROMIDES

Mark Rutland

The zeta potentials of monodisperse colloidal silica have been measured as a function of pH and as a function of the concentration of tetramethyl-, tetrapropyl-, and tetrapentyl- ammonium bromide in aqueous solution. The variation of the potential with pH was explained by a simple, point ion adsorption model from which a dissociation constant and Gibbs Free Energy of dissociation were obtained. By contrast, the results obtained with tetraalkyl ammonium ions could not be explained using this simple model. However, incorporation of a hydrophobic adsorption term and finite ion size in a more sophisticated model gave good agreement with experimental measurements. The validity of the model was supported by the reasonable dissociation constants which were obtained on fitting the experimental data. Dissociation constants and the corresponding Gibbs Free Energies have been calculated for both hydrophobic and site binding adsorption for each tetraalkyl ammonium ion. The stability of colloidal silica in solutions of these ions can now be satisfactorily explained in terms of the electrostatic repulsion between particles rather than a hydrophilic/hydrophobic solvation effect previously proposed.

ADSORPTION OF POLYDISPERSE NONIONIC SURFACTANTS AT THE SOLID/AQUEOUS INTERFACE

Jeff Aston

A high resolution capillary gas chromatography technique has been adapted to the analysis of polydisperse nonionic surfactants. This technique has

enabled the complete characterization of the oligomer distributions of very small samples of surfactants (typically 0.1 μg to 0.5 μg). It has made possible the determination of changes in the oligomer distribution on adsorption of surfactant at the solid/aqueous interface.

Isotherms have been measured for the adsorption of a series of polyoxyethylene nonylphenol surfactants from aqueous solution onto various solids. These isotherms indicate that the surfactant - surface interaction increases with an increase in the hydrophobicity of the adsorbent. They also show a dependence upon the average length of the ethylene oxide chain and the ratio of the surface area/solution volume. These latter factors affect both the total partition of surfactant between the surface and the solution, and also the selectivity of the solid surface.

A detailed study of the adsorption of N8 (a commercial nonionic surfactant) by a precipitated silica at various surface area/solution ratios, has been undertaken, where the equilibrium surfactant oligomer distributions in the adsorbed and solution phases have been determined. At surfactant concentrations above the critical micelle concentration, the phase separation approach has been used to estimate the surfactant oligomer distributions in free monomer solution and in micelles. This information has been combined with a surface phase model to interpret the results of the adsorption distribution studies.

THE CONDUCTIVITY AND DIELECTRIC RESPONSE OF COLLOIDAL DISPERSIONS

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The electrokinetic equations which describe colloidal phenomena have existed for some time. The theoretically defined Complex Conductance increment, $\Delta K^*(\omega)$, is a function of the colloidal properties; φ , the volume fraction of the colloid, a , the particle radius, $1/\kappa$ the Debye length, λ_1 , the ionic drag coefficients and ζ , the slipping plane potential. Separating $\Delta K^*(\omega)$ into its real and imaginary components, (the resistive and capacitive components of the experimentally measured impedance respectively) enables the evaluation of

$$\Delta K^*(\omega) + \sum \frac{\epsilon''(\omega)}{4\pi} \quad \text{and} \quad \Delta \epsilon'(\omega)$$

where $\Delta \epsilon'(\omega)$ and $\Delta \epsilon''(\omega)$ are the real and imaginary parts of the dielectric response of the system.

Using modern bridge techniques the frequency dependent Conductivity and Dielectric Response of colloidal systems in low electrolyte concentrations can be experimentally measured and thus the fundamental electrostatic equations upon which colloid theory is based can be further studied.

To date, any attempt to verify the theory experimentally has been fraught with difficulty not only in bridge design but in the production of 'ideal' colloidal systems for measurement. To this end we have constructed an accurate bridge system which enables one to measure the frequency response for low κa systems. Monodisperse polystyrene latices, properly cleaned and characterized have been used as the model colloid. For example, an amphoteric latex with an $i.e.p \approx 7$ was used, the ζ -potential being varied via the pH for κa 1.8, 2.9 and 9.8 systems.

Results for the low frequency conductance increment ($f = 1$ kHz) as a function of volume fraction and the Dielectric Response of these systems are in good agreement with the theory. Data for the above systems will be presented and experimental difficulties discussed.

REDUCTIVE DISSOLUTION OF HEMATITE IN THE PRESENCE OF ASCORBATE

Simon H.R. Davies

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This paper presents the results of a study of the dissolution of hematite (Fe_2O_3) in the presence of ascorbate. The results show that:

- (i) the rate of dissolution is greatly enhanced in the presence of ascorbate,
- (ii) the rate of reductive dissolution is proportional to the concentration of adsorbed ascorbate, and
- (iii) during the early stages of the experiment (0-30 hours) two moles of Fe(II) are dissolved for every mole of ascorbate oxidized.

In longer term experiments (> 100 hours) relatively more Fe(II) is dissolved, indicating that the intermediate oxidation product, dehydroascorbate, is also a reductant.

The rate of dissolution of hematite is much faster in the presence of both ascorbate and oxalate than in the presence of only one of these substances. In the presence of oxalate the dissolution rate is still proportional to the concentration of adsorbed ascorbate which suggests that oxalate, which forms strong Fe(II) complexes, assists the detachment of Fe(II) from the surface.

AGGREGATION OF COLLOIDAL SILVER

David Hayes

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Colloidal silver and gold sols have been the subject of much interest recently in the investigation of the surface enhanced Raman effect (SERS). Studies⁽¹⁾ have shown that the adsorption of pyridine derivatives and aggregation of the primary silver particles is necessary for the SERS effect to be observed.

We have undertaken studies to further investigate this aggregation. Optical absorption and electrophoresis measurements have been used to measure the rate of aggregation induced by 4-dimethyl-aminopyridine on silver sols (prepared by reduction with NaBH_4).

The results of these studies will be presented and the aggregation rates obtained will be compared with the predictions of DLVO theory.

- (1) S.M. Heard., F. Grieser, C.G. Barraclough and J.V. Sanders.
J.Coll.Int.Sci., 93,(1983),545.

SYNTHESIS OF COLLOIDAL CHALCOPYRITE

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A colloidal crystalline phase of chalcopyrite (CuFeS_2) has been successfully synthesised from solution. The procedure requires the prior precipitation of ferric hydroxide from a solution of ferric and cupric nitrates, and subsequent precipitation of the sulphide by addition of Na_2S . The preparation is carried out at 70°C under nitrogen.

The identity of the sulphide phase has been determined by XRD (X-ray diffraction), electron diffraction, electron microscopy and chemical analysis. Particle sizes of the mineral are in the range 5-9 nm.

The semiconductor nature of this mineral makes it suitable for photochemical experiments. Of particular interest is the possible role of chalcopyrite in the photochemical production of hydrogen.

The light dependence of dissolution processes will be investigated, in addition to the dependence of the rate of dissolution upon pH, complexing ligands and redox active species.

SURFACE ENERGETICS OF VICTORIAN BROWN COAL

Gregor Christie

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Significant improvements in the rheology of brown coal slurries can be achieved by modification of the brown coal structure. A range of new and modified Victorian brown coals have been characterised by H_2O adsorption isotherms. The modified brown coals can be slurried to concentrations greater than 60% wt/wt without the use of additives.

The energetics of the adsorbed H_2O layer on the brown coal was explored using a heat of wetting technique. Ampoules of coal were equilibrated with water vapour at various partial pressures. Simultaneously the water uptake was measured geometrically using an identical sample. The heat of immersion in water of the equilibrated ampoules of coal was measured by a microcalorimeter. The curve of heat of immersion with amount of water preadsorbed onto the coal and the water adsorption isotherm was determined.

A simple thermodynamically precise relationship exists relating the differential of the heat of immersion curve to the isosteric heat of adsorption. The entropy of the adsorbed layer can be calculated from the isosteric heat and the isotherm can be used to change the reference state to bulk water at 25°C .

The isosteric heat of adsorption and the entropy of the adsorbed layer at given water contents of the adsorbed layer can be accurately determined by this technique and can give an insight into water structure and the surface chemistry of such porous materials.

HIGH FREQUENCY DIELECTRIC DISPERSION OF A COLLOID

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There are two dielectric dispersions associated with colloidal material. The first of these occurs on a timescale of 1-10 MHz. Physically, this takes the form of a buildup of ion density at the rear of a particle. The second dispersion takes place at a much lower frequency 100-100 000 Hz. This dispersion is due to the diffusion of this charge density to the surrounding bulk electrolyte.

Recently, the high frequency dielectric dispersion has been described theoretically by R.W.O'Brien. This work is an experimental investigation of that theory.

Monodisperse polystyrene latices were selected as model suspensions. Dielectric measurements revealed an excellent agreement between theory and experiment. However, when a standard double layer model was used to calculate the zeta potential, the potential calculated was twice what was obtained from microelectrophoresis.

The effect of temperature was investigated. By changing the temperature, the relative permittivity of the background electrolyte could be changed. Excellent agreement between theory and experiment was obtained. However, the above experiment revealed a dramatic effect of temperature upon the double layer, in that as temperature increased the surface conductivity as opposed to the bulk conductivity became more important.

Dielectric measurements were also conducted on monodisperse aluminium phosphate sol. Although the theoretical fit was not as good as that obtained with polystyrene, the zeta potential calculated agreed with that obtained from microelectrophoresis.

SOLVATOCHROMIC ACID-BASE INDICATORS AS PROBES OF THE INTERFACIAL MICROENVIRONMENT OF MICELLES

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Four novel solvatochromic acid-base indicators, viz 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino) phenoxide, 1-hexadecyl-4-[(oxocyclohexadienylidene) ethylidene]-1,4-dihydropyridine, 1-hexadecyl-5-hydroxyquinoline and 1-hexadecyl-6-hydroxyquinoline (denoted $E_T(30)$, HOED, H5HQ and H6HQ), have been investigated in order to ascertain their suitability as probes of both the mean interfacial solvent properties and the electrostatic surface potentials, ψ_0 , of micelles in aqueous solution. It will be shown that in aqueous solutions of cationic micelles one of these solvatochromic indicators, $E_T(30)$, can be utilised to obtain a good estimate of the effective dielectric constant of the micellar interfacial microenvironment and a quantitative measure of the ψ_0 . The experimental ψ_0 estimates obtained with $E_T(30)$ in two well-characterized micellar systems, DTAB/NaBr and DTAC/NaCl, will be compared with the ψ_0 values calculated by assuming that (i) the micelles are monodisperse impenetrable spheres with a uniformly distributed surface charge, and (ii) the relationship between the micellar surface charge density and the ψ_0 can be given by the non-linearized form of the Poisson-Boltzmann equation. There are some problems associated with the use of HOED, H5HQ and H6HQ in aqueous micellar solutions and these will be briefly discussed.

APPLICATIONS OF FLUORESCENT PROBES FOR STUDYING MONOLAYERS AT THE AIR-WATER INTERFACE

Peter Triandos

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Fluorescence studies of acid-base reactions in air-water monolayers were made to investigate the effects of surface charge and water structuring at the air-water interface. The studies found that suppression of excited-state dissociation of 6-dodecyl-2-naphthol may be attributed to a reduced interfacial dielectric constant. Variation of the apparent pK_a with surface charge was studied with 4-heptadecyl-7-hydroxycoumarin and 5-(N-octadecanoyl) amino fluorescein and some qualitative comparison with theoretical models was made. The latter molecule was also used as a donor of excitation energy to 5-(N-hexadecanoyl) amino eosin as a way of studying energy transfer in two-dimensional arrays. The studies found that energy transfer occurred with a

dependence on distance different from that predicted by Forster theory in three-dimensional systems. Evidence for other transfer mechanisms was observed but could not yet be quantified due to problems associated with deconvolution of spectra.

ULTRAFILTRATION OF MULTI-COMPONENT NON-IONIC SURFACTANT SOLUTIONS

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The composition of a binary mixture of octa-ethylene glycol mono *n*-decyl ether ($C_{10}E_8$) and *n*-dodecyl glucopyranoside (DG) was determined as a function of total surfactant concentration by ultrafiltration. The filtrate was analyzed for both components of the mixture by G.C., to determine monomer concentrations of both species. Concentrations in the micellar phase were determined by mass balance. The more hydrophilic component of the two surfactants, ($C_{10}E_8$), was observed to have an increasing monomer concentration after the onset of micellization. The opposite was observed for DG.

The experimental results were compared to a phase separation, ideal mixing model of micellization developed elsewhere¹, and was in good agreement on both quantitative and qualitative bases.

References:

1. Clint, J.H., J.Chem.Soc., Trans. Faraday 1, 1975, 71, 1327.

PURITY AND PURIFICATION OF SINGLE COMPONENT SURFACTANT SOLUTIONS BELOW THE C.M.C.

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Any research studying the surface of surfactant solutions should check that the surface doesn't contain highly surface-active impurities. Effective criteria for assessing surface purity are the absence of hysteresis of the surface tension, and attainment of constant surface tension in a relatively short period of time. These criteria can only be determined by monitoring surface tension, immediately after a rapid compression and expansion of the surface of the surfactant solution.

To attain this level of purity, one must firstly purify the surfactant material as much as possible by bulk purification methods, and only then use

surface purifying methods, such methods being chromatography, foaming, adsorption by Al_2O_3 (acidic) and removal of the surface by suction. However, all these methods give a low recovery rate of the main surfactant component. Therefore, methods of purification giving good recovery will be investigated in the future.

MEASUREMENT OF THE MICROENVIRONMENT AT THE AIR-WATER INTERFACE

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Several fluorescent probes (N-Dansyldihexa- decylamine, 1-acetylpyrene, 1-pyrenecarboxaldehyde, 1-pyrenedodecanoic acid) were diluted into several monolayer systems to see if properties such as effective "polarity" and viscosity could be related to changes in surface pressure as the monolayer was compressed. Even though it was not possible to observe changes in the host monolayers, the probes exhibited their own properties and these were related to changes in surface pressure. From this it was possible to relate changes in molecular orientation of the probes themselves with changes in surface pressure.

Relaxation of surface pressure with time also seemed an important process governing monolayer systems. A detailed investigation of a 20 mole % N-Dansyldihexadecylamine in stearic acid monolayer over pure water showed the presence of two relaxation processes. The initial more rapid process only occurs below about 0.20 nm^2 .

INVESTIGATION OF EQUILIBRIUM WETTING FILMS

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When you have a closed system which consists of a solid and a liquid, with a partial vapour pressure p/p^0 , the vapour molecules interact with the solid. If the interaction free energy is lowered by adsorption of the vapour molecules onto the solid, a wetting liquid film will form.

The equilibrium film thickness can be measured by ellipsometry as a function of partial vapour pressure. For non-polar films, the Lifshitz theory gives the predicted results for such systems.

Preliminary results for the adsorption of pentane on mica were presented and compared to the theoretical isotherms. The oscillator model was

used for the calculation of the mica dielectric function. A Lorentzian equation also used for the prediction of this dielectric function showed little difference to that predicted by the oscillator model.

The experimental isotherm gave film thicknesses vastly greater than those expected from theoretical calculations. Possible reasons for the discrepancy are that equilibrium was not attained or that there was a temperature gradient between the mica and the pressure transducer during the experiment which would lead to large film thicknesses. It is also possible that, if there were no experimental artifacts, there is a large contribution to the disjoining pressure from the structural component.

Further experimentation is necessary before any firm conclusions can be drawn.

THIN FILMS AND MOVEMENT OF THE THREE PHASE LINE OF CONTACT

Gayle Newcombe SAIT

The process of mineral flotation involves three basic steps:

- i) the mineral particle and air bubble must collide,
- ii) the thin liquid film between them must thin and eventually rupture,
- iii) the area of direct contact between the gas and solid must expand to a radius large enough to ensure that the aggregate is strong enough to withstand the turbulence of the flotation cell.

Step iii) has been studied on chemically modified silica surfaces over a range of equilibrium contact angles.

The study involved pressing an air bubble against a modified silica plate and filming the expansion of the area of contact after rupture of the thin film. The velocity of the boundary of contact and the contact angles formed during the movement were of particular interest.

It was found that, for the surfaces studied, the relationship between the velocity of the boundary and the dynamic contact angle could be predicted if the equilibrium contact angle was known.

It was also found that the method of prediction could be used in other experimental situations, eg. movement of an air/water meniscus in a capillary, as long as the equilibrium contact angle was known.

DIRECT MEASUREMENT OF FORCES IN SURFACTANT AND NaCl SOLUTIONS

Patty McGuigan

Forces between mica surfaces in aqueous surfactant and NaCl solutions are reported. These forces are directly measured using the surface forces apparatus as designed by J. Israelachvili.

In the surfactant systems studied, CTAB and dihexadecyldimethyl ammonium acetate, the cationic surfactant is adsorbed from solution on the negatively charged mica surfaces as either a monolayer or bilayer. These force measurements can be fitted to exact P.B. theory. The Debye length of these surfactant solutions can be calculated by assuming only "free" counterions and monomers contribute to the forces when the surfaces are positively charged and positively charged aggregates determine the Debye length when the surfaces are negatively charged. The surface charge also agrees with this dissociation.

In concentrated NaCl solutions, an extra force is present between the mica surfaces which do not fit the P-B theory. An oscillatory force with steps of about 0.3 - 0.35 nm is measured and this is superimposed on a monotonic hydration force. The addition of urea, thought to be a structure breaker, appears to have little effect on the stepped structure.

LIGHT SCATTERING STUDIES ON VESICLES IN DIDODECYLDIMETHYLAMMONIUM HYDROXIDE

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Australian National University

Systematic measurements of light scattering on DDAOH/water solutions have been performed in the concentration range 10^{-5} to 10^{-3} M. Scattering of light is dominated by large objects, whose concentration increases monotonically with the concentration of surfactant. Assuming that these objects are unilamellar vesicles their size and concentration may be determined. In all the cases the experimental data fit well with the model assuming a vesicle radius of 100 ± 5 nm.

The determined vesicle concentration is very small. About 1 out of 1000 surfactant molecules aggregates in vesicles. This is in agreement with the results of direct observation with an ultramicroscope.

The vesicle size determined by freeze fracture electron microscopy (60 ± 10 nm) is 40% smaller than that deduced from light scattering data. The

vesicle concentration increases nonlinearly with the surfactant concentration.

CELL ADHESION

Geoff Francis

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A new device is described in which an accurately measured force is applied to individual adherent cells while the topography of the adhesion zone is simultaneously monitored. The force is applied via a flexible glass micropipette, attached by suction to the cell under study, and is calculated directly from the measured pipette deflection. Regions of close contact in the adhesion zone are observed using interference reflection microscopy. The device has been used to measure the force required to detach human red blood cells from hydrophobic and hydrophilic glass surfaces, and to detach Dictyostelium discoideum amoebae from a hydrophobic glass surface. The measured forces per unit length of contact perimeter are within an order of magnitude of the tensions required for membrane rupture.

OIL FLOTATION OF FINE SULPHIDE MINERAL PARTICLES

George Levay

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Very fine mineral particles (less than 10 μm) are difficult to float in conventional froth flotation processes. Today there is considerable interest in developing methods for the recovery of fine mineral particles.

Recovery and separation experiments of fine ($\sim 2 \mu\text{m}$) galena, chalcopyrite and sphalerite mineral particles and their mixtures with quartz were performed in the presence of small oil droplets. Only pure oil was used. No polymeric stabilizer was present. The techniques and apparatus have been described.

The effect of pH, volume of oil, mineral pulp density and head grade of mixtures on the separation, recovery and final grade was investigated.

The experimental results show that:

- the recovery of fine sulphide mineral particles with oil is pH dependent.
- the selectivity of recovery is pH dependent.
- very good recovery and selectivity is obtained when low head grade

mixtures of sulphides and quartz are used.

- to obtain high recovery it is necessary to break the oil down into as many small droplets as possible to provide a large surface area for collection of fine solid particles.

Experimental trials on the Mt. Isa Mines Pb/Zn concentrator, heavy Medium Plant Slimes show that a small addition of oil (2 kg/t) to the standard froth flotation test produces a dramatic increase in the rate of flotation; the recovery of silver increases by 10% and the recovery of lead increases by 8% without any effect on selectivity.

FLOTATION OF QUARTZ BY DOUBLE-CHAINED QUATERNARY AMMONIUM ION SURFACTANTS

William Ducker

Australian National University

The froth flotation of ground quartz and ballotini glass spheres using the collector dihexadecyldimethylammonium acetate (DHDAA) was examined using a Hallimond tube. Large differences in the flotation properties of these two indicated that ballotini spheres are not a good substrate for the study of the flotation of ground minerals. The explanation originally proposed by Anfruns and Kitchener, that this difference was due to surface roughness, stimulated the study of an unusual surfactant, methyltriethylammonium bromide (MTHAB) which was specifically chosen to adsorb onto the rough sections of quartz particles. Flotation experiments using both MTHAB and DHDAA demonstrated that while the addition of MTHAB caused no change to the flotation of ballotini spheres it substantially improved the flotation of quartz. Unfortunately, however, attempts to directly attribute this behaviour to the adsorption of MTHAB on the angular sections of quartz were inconclusive.

In addition, the discovery that the adsorption of DHDAA to the solution-air interface is relatively slow and only occurs in measurable amounts from solutions more concentrated than 10^{-5} M, enabled an assessment of the importance to flotation of adsorption to this interface. Experiments reported here indicate that contrary to current belief, adsorption of surfactant at the air-solution interface is not a determinant of flotation at concentrations above which a bilayer is adsorbed at the particle surface.

EFFECT OF NaCl ON THE ADSORPTION OF TRACE ELEMENTS ONTO
GOETHITE

Kaye Green

Bendigo C.A.E.

Salt damaged land is a costly problem in northern and western Victoria. Besides the obvious damage to the soil structure, salts also effect the solubility, and hence availability, of some trace elements in the soil. Goethite was used to test the solubility of 10^{-4} M zinc, copper cobalt and cadmium in the presence of NaCl concentration $>10^{-2}$ M. The adsorption of the first two trace elements increases in acid solution and so they are less available to plants. Cobalt adsorption was unaffected by various concentrations of NaCl solution, but the toxic trace element, cadmium, became more available as the adsorption decreased in salt solution at pH values around 8.

CHARACTERISATION OF COLLOIDAL PARTICLES BY SEDIMENTATION
FIELD FLOW FRACTIONATION

Geoff Nicholson

Water Studies Centre

Chisholm Institute of Technology

The WSC at Chisholm has been studying the behaviour of suspended particulate matter (SPM) within normal aquatic systems for some years. SPM plays a dominant role in the transport and fate of trace metals and organic contaminants within rivers, estuaries and oceans.

The colloidal size range ($< 1 \mu\text{m}$) in particular, because of its large specific surface area, is an important component of SPM. Unfortunately, at present it has not been well served by any convenient methods of analysis.

Sedimentation Field Flow Fractionation (SFFF) is a promising new technique for the separation and analysis of the colloidal fraction. It is a long, thin channel chromatographic-like flow elution technique based on Field Flow Fractionation principles developed by Calvin Giddings over 20 years ago, specifically for the analysis of macromolecules. In SFFF the channel is formed by the clamping together of two Cr-Ni alloy stainless steel alloy ribbons, separated by a nylon gasket with the channel shape cut out. The ribbons are looped into a circle and placed within a centrifuge basket. The channel dimensions are 93.1 cm from inlet to outlet, 1.7 cm wide and 0.025 cm thick.

A parabolic flow profile is formed as the carrier solution is passed through, and particle interaction with the centrifugal force and the velocity profiles of the carrier cause particle size separation. The resolution is excellent, the technique is theoretically exact, fragile structures can be studied, and fractions can be collected.

ELECTROSTATICS ON MEMBRANE SURFACES

Janine Kibblewhite

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The electrostatic surface potentials of a number of different cationic micelles have been measured using the solvatochromic acid-base indicator $E_T(30)$. The surface potentials were varied by changing the concentration of added pentanol. The experimental surface potential estimates have been compared with those obtained by numerically solving the non-linearized form of the Poisson-Boltzmann equation. The results indicate that the degree of counterion binding decreases with increasing pentanol concentration. Both the calculated and experimental surface potentials have been found to decrease with increasing pentanol concentration.

CONDUCTIVITIES OF MICELLES

Celestino Carosella

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The system studied in this work was that of the well characterised micelles of sodium dodecyl sulphate (SDS). SDS conductivities were measured in various sodium chloride electrolyte concentrations from which a value for the conductivity increment

$[K^* - K^\infty] / \varphi K^\infty$ was obtained.

The theory describing the conductivity of a dilute colloid in a symmetric electrolyte was remodelled to take into account the effect of ion binding at the surface of the micelle. This made it possible to obtain theoretical predictions for the conductivity increments and compare them with those found experimentally, enabling evaluation of the magnitude of the ion binding. The theory was found to predict binding constants (α values) quite well within a concentration range.

A STABILITY MODEL FOR CONCENTRATED DISPERSIONS

Anne Lombard

In a recent patent [Australian Patent AU-A-37086/84, "Liquid Detergent Compositions"] the stabilisation of phosphate/silicate crystals, in a laundry liquid composition, by 'space filling' flocs or aggregates of surfactant called spherulites was described.

A Transmission Electron Microscopy study of similar compositions after freeze fracture indicated that the majority of the composition does not contain spherulites, i.e. they are not 'space filling'.

Therefore for the compositions we tried the stabilising mechanism outlined above does not appear to hold.