PROCEEDINGS AND ABSTRACTS

OF THE TWELFTH

AUSTRALIAN COLLIOD AND SURFACE CHEMISTRY

STUDENT CONFERENCE

detector response

retention time

(a)

1EO
2EO
3EO
4EO
5EO
6EO
7EO
8EO
9EO
10EO
11EO
12EO
13EO
14EO

(b)

8EO

(c)

8EO
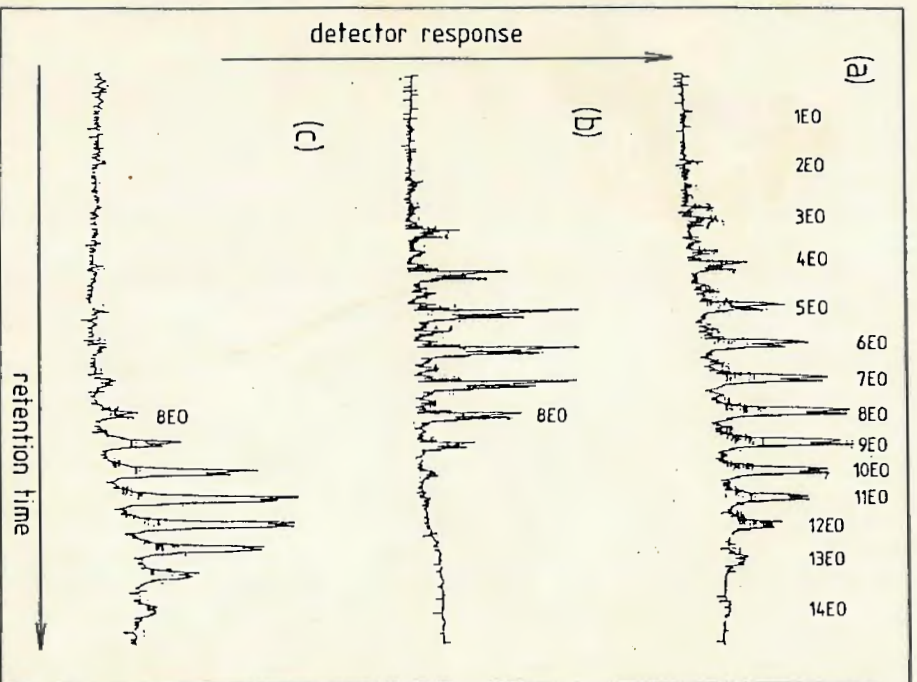
PROCEEDINGS AND ABSTRACTS

OF THE TWELFTH

AUSTRALIAN COLLOID AND SURFACE CHEMISTRY

STUDENT CONFERENCE

ROSEWORTHY AGRICULTURAL COLLEGE, 1985

CONTENTS

ACKNOWLEDGEMENTS

Special Note

Information on the Australian Colloid and Surface Chemistry Student
Conference may be obtained from:

> Associate Professor R.J. Hunter
>
> Department of Physical Chemistry
>
> University of Sydney
>
> SYDNEY
>
> NSW   2006
>
> Australia

> or

> Professor T.W. Healy
>
> Department of Physical Chemistry
>
> University of Melbourne
>
> PARKVILLE
>
> Victoria   3052
>
> Australia

Cover:

Gas chromatograms of a non-ionic surfactant of mixed composition
(nominally 8-ethylene oxide residues).   (a) is the original
surfactant and (b) and (c) show its partitioning between hexane and
water respectively.

"A smattering of everything, and a knowledge of much"
[with apologies to Dickens].

PREFACE

The Twelfth Australian Colloid and Surface Chemistry Student
Conference was held in Adelaide in February 1985. The Abstracts
appearing in this booklet were prepared by postgraduate students
from the Australian National University, Melbourne, Monash and
Sydney Universities, Chisolm Institute of Technology and the South
Australian Institute of Technology. These students all delivered
papers at the Conference.

The first formal Student Conference was held in Sydney in 1968,
growing out of earlier, informal discussions between the research
groups at the Universities of Melbourne and Sydney, led by those two
stalwarts of Australian Colloid Science, Tom Healy and Bob Hunter.
Much is expected of a student who presents a paper at these
Conferences - the standard is expected to be high and the student
must anticipate receiving extensive criticism of his or her work.
Since Australia is arguably the world leader in Colloid Science in
the majority of theoretical and experimental areas, the postgraduate
students really have an impressive yardstick with which to measure
their efforts. The intense scientific milieu, which is
characteristic of these Student Conferences, is maintained over a
three to four day period, not infrequently at the bar!

The School of Chemical Technology, South Australian Institute of Technology hosted this Twelfth Conference. Registration, lunch and several talks were held at the Levels Campus after which the participants travelled northwards to spend three days at Roseworthy Agricultural College. Here, in a splendid environment, the participants relaxed and engaged one another in that frank and open scientific debate which is a hallmark of Australian Colloid Science.

Once again we were fortunate to have an overseas guest of honour to give the Conference Address. On this occasion it was Dr. Luuk Koopal, Reader in Colloid and Surface Chemistry from The Agricultural University in Wageningen, The Netherlands. Luuk spent twelve months sabbatical leave (July 84 - July 85) in the School of Chemical Technology at S.A.I.T. We thank him warmly for his speech, for his good humour and for his scientific efforts whilst in our country.

Suffice it to say that the standard of papers at this Twelfth Student Conference was high - in fact the level has increased in depth and breadth over the years, for groups have sprung up all over the continent.

Each Conference owes its success in a large part to the efforts of a key student at the host institution. On this occasion the mantle fell on the shoulders of Robert Hayes at S.A.I.T. Thank you, Rob, from all of us.

John Ralston,

Adelaide 1985.

PARTICIPANTS - 1985

Guest of Honour

Dr. L.K. Koopal (Agricultural University, The Netherlands)

From the Australian National University

Staff	Students
Dr. H. Christenson;	J. Marra
Prof. J. Israelachvili;	
Dr. R. Pashley.	

From the Chisolm Institute of Technology

Staff	Students
Dr. R. Beckett.	G. Nicholson.

From the South Australian Institute of Technology

Staff	Students	
Miss G. Newcombe;	M. Bannear;	G.Levay
Mr. K. Quast;	R. Crawford;	D.Price
Prof. J. Ralston.	R. Hayes;	D.Readett.

From the University of Melbourne

Staff	Students	
Dr. D. Chan;	G. Allan;	D. Hayes;
Dr. F. Grieser;	A. Burgess;	M. Lay;
Prof. T.W. Healy;	N. DeGuingand;	Y. Leong;
Prof. L.R. White;	C. Drummond;	J. Lum Wan;
	D. Dunstan;	P. Mulvaney;
	M. Gee;	D. Nguyen;
	J. Godfrey;	P. Scales;
	G. Hartland;	R. Sheers.

From the University of Sydney

Staff	Students
Assoc. Prof. R.J. Hunter;	D. Gray;
Dr. B. Midmore.	I. Harrison;
	R. Vegners.

From Monash University

Students

A. Hilderbrand.

VISITORS

Albright and Wilson, VIC.

Mr. S. Clark

BHP Central Research Laboratories, N.S.W.

Dr. A. Torrance

Bougainville Copper Ltd., S.A.

Dr. N.C. Clarke

CSIRO (Applied Chemistry)

Dr. D.N. Furlong

CSIRO (Mineral Chemistry)

Dr. P. Smith

Dominant (Aust.) Pty Ltd., S.A.

Mr. C. Astley

Sola Optical Australia Pty. Ltd., S.A.

Dr. K.J. Pidgeon

TWELFTH AUSTRALIAN COLLOID STUDENT CONFERENCE

FEBRUARY 1985, ROSEWORTHY SA

PROGRAMME

Opening Session

Wednesday 13/2/85

11.00am   Commencement of Registration at School of Chemical
           Technology, Levels Campus, S.A.I.T.

12.15 pm   LUNCH

           Chairman: Prof. John Ralston

2.30 pm   Dr. Brian Midmore, University of Sydney
           "Cellulose as a Polyelectrolyte"

3.00 pm   Geoff Nicholson, Chisholm Institute of Technology.
           "The contrast of simulated estuarine induced
           coagulation of particles in:
           (a) Redwater Creek, an organic rich, low mineral
           content water body;
           (b) Yarra River, a mineral rich, low organic content
           water body"

3.25 pm   Ian Harrison, University of Sydney
           "Movement of Fluoride in Soils and Sediments"

4.00 pm   Buses arrive to transport conference participants north
           to Roseworthy Agricultural College, the 'live-in' site
           for the conference.

Thursday 14th

           Chairman: Professor John Ralston

9.00 am   David J. Gray, University of Sydney
           "Interaction of Iron Oxides with Clays as revealed by
           High Gradient Magnetic Separation"

9.25 am   George Levay, School of Chemical Technology, S.A.I.T.
           "Detection and Removal of Chlorinated Hydrocarbons from
           Water"

9.50 am   Rob Hayes, School of Chemical Technology, S.A.I.T.
           "Sulphide Minerals: Floatability as a Function of E_h
           andParticle Size"

10.15 am   David Price, School of Chemical Technology, S.A.I.T.
            "Significance of Multicomponent Behaviour in Flotation
            Practice"

10.40 am   Morning Coffee

            Chairman: Professor Tom Healy

11.15 am   Paul Mulvaney, University of Melbourne
            "The Photodissolution of Colloidal Cadmium Sulphide:
            Effect of Metal Ion Adsorption"

11.40 am   Michael Bannear, School of Matallurgy, S.A.I.T.
            "Mechanisms of Metal-Ion Activation of Sphalerite"

12.05 pm   Ray Vegners, University of Sydney
            "Colloidal Carbon and Silica: Their Use in Solar Energy
            Collectors and Anti-Reflectance Coatings"

12.30 pm   Michelle Gee, University of Melbourne
            "Thin Films"

1.00 pm   Lunch

            Chairman: Dr.Franz Grieser

2.30 pm   N. De Guingand, University of Melbourne
            "Thickening of Flocculated Slurries"

2.55 pm   David Readett, School of Metallurgy, S.A.I.T.
            "Surface Chemistry of Lignite"

3.20 pm   Greg Hartland, University of Melbourne
            "Experimental and Theoretical Aspects of the Surface
            Potential of Ionic Micelles"

3.45 pm   Peter Scales, University of Melbourne
            "Radial Flow Streaming Potential Measurements on Flat
            Plates"

4.10 pm   David Dunstan, University of Melbourne
            "The Conductivity of Dilute Colloidal Dispersions"

Friday 15th

            Chairman: Professor Jacob Israelachvili

9.00 am   Russell Crawford, S.I.T./S.A.I.T.
            "Floatability of Tailored Quartz Particles"

9.25 am   Johan Marra, Australian National University
            "Forces between lipid bilayers"

9.50 am   Anna Burgess, University of Melbourne
            "A Monte-Carlo Study of Adsorption of Water Vapour on
            Quartz"

10.15 am   Judith Lum Wan, University of Melbourne
                  "A Method of Calculating the Site Energy Distribution
                  of a Heterogeneous Surface"

10.40 am   Morning Coffee

                  Chairman: Assoc.Professor Bob Hunter

11.15 am   Y.K. Leong, University of Melbourne
                  "Rheology of Brown Coal Suspensions"

11.40 am   David Everett, University of Sydney
                  "Viscous and Elastic Properties of Coagulated Colloidal
                  Dispersions"(withdrawn)

12.05 pm   Calum Drummond, University of Melbourne
                  "Acid-Base Indicators as Probes of the Interfacial
                  Microenvironment of Nonionic Micelles"

12.30 pm   David Hayes, University of Melbourne
                  "Laser Doppler Electrophoresis"

1.00 pm   Lunch

2.00 pm   Afternoon free for recreational activities

6.00 pm   Wine Tasting

                  Conference Dinner
                  Guest Speaker: Visiting Professor Luuk Koopal
                  (Agricultural University, Wageningen, The Netherlands)

Saturday 16th

                  Chairman: Professor Lee White

9.30 am   Janine Godfrey, University of Melbourne
                  "Attenuated Total Reflectance (ATR) Studies of Model
                  Solid-Aqueous Interfaces"

9.55 am   Matt Lay, University of Melbourne
                  "Some Aspects of Prototropic Reactions at Interfaces"

10.20 am   Morning Coffee

10.45 am   Greg Allan, University of Melbourne
                  "The   Partitioning   of   Polydisperse   Non-Ionic
                  Surfactants Between Oil and Water"

11.10 am   Robert Sheers, University of Melbourne
                  "Adsorption of Organic Molecules at the Solid Aqueous
                  Interface"

12.00   Lunch
Midday

1.30 pm   Departure from Roseworthy to Adelaide by bus.

ABSTRACTS

CELLULOSE AS A POLYELECTROLYTE

B.R. Midmore

Charge/pH isotherms at 25°C for cotton linters, bleached sulphate pulp, and unbleached sulphate pulp were obtained (varying electrolyte concentration and the counterion) using a titration technique originally developed for studying AgI and metal oxide sols. The p.z.c. for these pulps was thereby obtained. These curves were analysed using polyelectrolyte theory and the acidic group was shown to be a carboxyl group at the C_6 position. The charge density was calculated by determining the specific surface areas using negative adsorption, the low charge being corrected. The effect of double layer overlap was also investigated for the unbleached sulphate pulp. These areas were compared with those obtained from nitrogen adsorption using a solvent exchange technique. Electrokinetic measurements were made on the bleached sulphate pulp and cotton linters using streaming potential and electrophoresis techniques. Zeta (as a function of pH and electrolyte concentration) and the isoelectric point were so obtained. Estimates of the effective surface potential were made using:-

1. The Gouy-Chapman equation assuming $\sigma_O = \sigma_\delta$.
2. The negative adsorption data using an estimate for S.
3. Polyelectrolyte theory.

COAGULATION OF NATURAL AQUATIC PARTICULATES

Geoff Nicholson

The coagulation behaviour of two different types of streams was studied. The Yarra River is quite turbid and its particulates are dominated by mineral particles. Redwater Creek is non-turbid, but highly coloured, due to an unusually high concentration of organic humic substances. The rate and extent of coagulation was monitored by the Fe concentrations in filtered river water. The coagulation inducing reagents were $CaCl_2$, $Ca(NO_3)_2$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, and NaCl. In most cases the coagulation process was essentially complete within one hour, although there were exceptions to this trend and there was some evidence for slow coagulation continuing. The coagulation efficiency with $CaCl_2$, $MgCl_2$ and NaCl in both waters at pH 7 was in the order Ca > Mg >> Na. It appeared that specific adsorption was a major mechanism in lowering the particulate surface charge in the case of Ca and Mg, with Ca being more strongly adsorbed. A significantly lower precentage of the total Fe was removed by coagulation in Redwater Creek than for Yarra River water. Colloidal Fe may be stabilized more by the higher levels of humic matter in Redwater Creek by electrostatic or steric stabilization, or the Fe could be held in solution by complexation to organic fractions which are not aggregated by electrolytes.

There appeared to be a trend for $MgSO_4$ to be significantly less effective than $MgCl_2$ or $Mg(NO_3)_2$ in coagulating both types of river water. This may be due to the adsoprtion of sulphate ions onto the surface of Fe colloids. The aggregation of Fe in both waters in the

presence of electrolytes increased with increasing pH in the range 5 - 8, and was probably due to the decreased co-ordination of metal ions to ligand groups in the organic compounds associated with the Fe as the pH is lowered.

The settlability of aggregates was measured and in direct comparison with sample refiltrations at equivalent reagent concentrations, only two-thirds of the amount of filterable Fe was removed by settling. This could have significance in determining the efficiency of trapping coagulated colloidal material in estuarine systems.

MOVEMENT OF FLUORIDE IN SOILS AND SEDIMENTS

I.W. Harrison
Department of Soil Science
University of Sydney

The amount and distribution of total and water-soluble fluoride in the soils and sediments in the vicinity of the Kurri-Kurri aluminium smelter was determined. The concentration of water-soluble F in the surface soil ranged between $2-5\mu g \ g^{-1}$ soil for all sites, while total F was between $50-150\mu g \ g^{-1}$; the corresponding amounts for lake and stream sediments were $2-70$ and $250-1000\mu g \ g^{-1}$ respectively. The surface soils contained the maxiumum concentrations of F in all profiles and this decreased with depth, suggesting that F had moved downwards. A similar trend was observed for sediments, except that F had penetrated to a lesser extent than in soils.

The soil studied was of yellow podzolic type with sandy loam surface

soil and medium clay subsoil of low hydraulic conductivity. Most of the F was found in the A horizon but the possibility exists for this to move laterally in the perched water table that develops after heavy rain.

An area sprayed with F-containing waters was found to contain water-soluble F ($>1.0\mu g$ g^{-1} soil) down to a depth of 70cm. Concentrations of $>1.0\mu g$ g^{-1} soil are considered to be indicative of F contamination.

Desorption studies revealed that virtually all F desorption occurs within an extraction period of 1 hour for soil: solution ratios that are likely to be encountered in the soil. Slow reactions are relatively unimportant in this situation.

Results from extraction and leaching experiments indicated that much of the F added to the spray irrigation area can be desorbed by water. It is estimated that 40% of the F added to the upper 5cm of this profile would be desorbed by the action of rainfall over a period of approximately 10 years.

INTERACTION OF IRON OXIDES WITH CLAYS AS REVEALED BY HIGH GRADIENT MAGNETIC SEPARATION

D.J. Gray

Department of Soil Science, University of Sydney

High Gradient Magnetic Separation (HGMS) can be used to concentrate

paramagnetic materials such as the soil iron oxides goethite and hematite. The process involves separation of the sample into a magnetically retained fraction and a non-magnetic residual. Schulze and Dixon (1982)[Soil Sci. Soc. Am. J. 13: 793-799] reported magnetic fractions equal to 13-33% of the original sample by weight, in which the iron oxides have been concentrated 205 times.

In this work the HGMS treatment of samples from a soil site at Nabarlek, Northern Territory, is described. The soil is a lateritic podzolic, with a sandy A horizon containing 7% clay, overlying an iron oxide rich B horizon with 40% clay. Samples of the ($2\mu m$ material from the A and B horizons were concentrated.

In the A horizon up to 85% of the material was magnetically retained with no observable concentration of the iron oxide. This suggests that the iron oxide is so strongly associated with the clay matrix that the HGMS procedure could not separate the two phases. In the B horizon 10-40% of the material was magnetically retained with a concentration of iron oxides of 1.3-1.9 times in the retained fraction, relative to the original sample. The iron oxides are less strongly associated with the clay matrix, allowing concentration to occur.

Major differences in the association of iron oxides with clay in the two horizons of this duplex soil are observed. Iron oxides in the A horizon could not be concentrated by HGMS, a phenomenom not previously reported.

DETECTION AND REMOVAL OF CHLORINATED HYDROCARDONS FROM WATER

George Levay

School of Chemical Technology, S.A.I.T.

In analyzing organic material in water, two different approaches are possible. The first uses specific analysis of organic micropollutants, by means of gas chromatography and mass spectrometry.

The second approach involves surrogate, collective or group parameters, such as total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), total organic halogen (TOX), U.V. absorbance or fluorescence.

The adsorption method for determination of total organic halogen (TOX) is presented.

Two types of processes which offer the greatest promise of solving drinking water treatment problems are described:

-oxidation processes using chemical oxidants such as ozone or chlorine, or biological oxidation alone or in combination with chemical oxidation.

-adsorption processes using granular activated carbon filters alone or combined with biological oxidation.

SULPHIDE MINERALS; FLOTATION RESPONSE AS A FUNCTION OF REDOX POTENTIAL (E_h) AND PARTICLE SIZE

Rob Hayes

School of Chemical Technology, S.A.I.T.

It has been observed that the flotation response of chalcopyrite (CuFeS$_2$) can be manipulated by adjusting the redox potential of the flotation pulp – [W.J. Trahar, Int J. Min. Proc., 11, 57 (1983)].

This observation inplies the production of a hydrophobic oxidation product at the mineral surface. An obvious candidate is elemental sulphur (S°). However, this species has not been experimentally identified, possibly because of the difficulty involved in low-level S° determination.

In the work already completed, galena (PbS) has also been shown to qualitatively exhibit similar flotation response /E_h behaviour to that observed for chalcopyrite. This effect, and its relationship with the particle size of the mineral, will be investigated quantitatively using a laboratory scale flotation cell (Hallimond Tube) for the minerals galena, chalcopyrite and sphalerite ($\overline{Z}nS$).

The identity and nature of the hydrophobic oxidation product will be investigate spectroscopically.

SIGNIFICANCE OF MULTICOMPONENT BEHAVIOUR IN FLOTATION PRACTICE

David Price

School of Chemical Technology, S.A.I.T.

Conventionally, research efforts in flotation have emphasized the

chemical nature of the mineral surface and the effect of adsorbed species. Until recently little work has focussed on the kinetics and thermodynamics of the flotation process. Analysis of the rate constant, k, and oxidation/reduction considerations can account for a series of rate constants, hence differences in recovery behaviours. Preliminary work at Mt. Isa Mines indicates multicomponent behaviour, hence a need to identify and partition particles according to rate constants.

THE PHOTODISSOLUTION OF COLLOIDAL CADMIUM SULPHIDE: EFFECT OF METAL ION ADSORPTION

Paul Mulvaney

The effect of adsorption of metal hydroxides upon the cadmium sulphide surface was investigated. Inhibition of photocorrosion was found for the transition metals Co(II), Ni(II) and Zn(II) but not Cd(II).

Solution species (e.g. O_2) were shown to be prevented from participating in surface redox reactions. A model was proposed to account for the behaviour of Cd(II) which suggests instability against cathodic decomposition. Hole scavenging by adsorbed metal hydroxides did not occur. Co(II) and Ni(II) were found to catalyse the formation of hydrogen peroxide rather than oxygen when present in homogeneous water photolysis systems.

MECHANISMS OF METAL ION ACTIVATION OF SPHALERITE

M.A. Bannear

The mechanisms involved during the metal-ion activation of sphalerite by copper and cadmium were examined by use of adsorption and electrokinetic studies. A high surface area synthetic sphalerite sample was used for all test work. Results have shown that the mechanism involved is far more complex than the traditional ion exchange theory. Exchange ratios have been used as the basis for determining to what extent other reactions are involved in the overall activating effect. A reductive adsorption occurs to a significant extent with copper activation, which involves a redox couple where ZnS is oxidised to elemental sulphur and simultaneously dissolved oxygen and Cu (II) are reduced. Cadmium activation of sphalerite appears to be largely controlled by diffusion of species through the CdS surface layer.

COLLOIDAL CARBON AND SILICA: THEIR USE IN SOLAR ENERGY COLLECTORS AND ANTI-REFLECTION COATINGS

Ray Vegners

Studies were undertaken to optimise the ratio of colloidal carbon to colloidal silica in thin films on top of copper in order to fabricate highly efficient photothermal solar selective coatings. The application of these colloidal coatings involved the dipping of copper coated glass slides into a bath containing colloidal carbon (plus surfactant), colloidal silica, water and acetone. Varying the

withdrawal rate and the acetone concentration led to varying film thicknesses. The acetone was required to produce even, thin films.

The investigation of the effective solar absorptance (calculated at 150°C) as a function of the carbon to silica ratio and film thickness indicated that the optimum coating had a silica to carbon weight ratio of 1 : 1 at a thickness between 450nm to 500nm and an effective solar absorptance of 0.771. These coatings were also found to be stable at temperatures of 500°C in vacuo. Theoretical calculations (Maxwell Garnett equation) however, suggest that more highly efficient coatings could be fabricated if the carbon colloids were more dispersed in the coatings.

Studies done on colloidal silica anti-reflection coatings have shown that the optimum density of the films is dependent on the primary particle size of the silica colloids. The experimental results suggest that a coating consisting of colloidal silica with a primary particle diameter around 45nm may produce an anti-reflection film, on glass, with 99% solar transmittance. Alternatively, a mixture of small and large silica colloids may also achieve this.

THIN FILMS

Michelle Gee

The static and dynamic properties of thin liquid films will be discussed. Optical methods used in the investigation of these

properties, in particular ellipsometry and light-scattering, will be presented.

SEDIMENTATION AND FLOCCULATION OF SLURRIES

N.J. E. de Guingand

The disposal of bauxite residue, a waste product produced prolifically in the Alumina industry may be improved by employing a deep cone thickener. My project's major aim is to optimise the operating conditions of a deep cone thickener, for Alcoa, by examining the aspects of sedimentation, flocculation and rheology.

The action of thickening involves 3 zones; the top zone is the clarification zone, then the hindered settling zone and the compression zone. Deep thickeners have recently been developed to utilise the compression zone. A lattice structure is formed in this zone which provides a resistance to any concentration increases. The lattice can only be broken by application of a normal stress, applied by increasing the mass of solids above it. When the weight of these solids becomes greater than the compressive yield stress ($P_c(\phi)$) of the lattice it will break and another will form with a new, higher P_c which will, in turn, break so that a continuous process ensues. The rate at which the system responds to the applied pressure can be indicated by the dynamic compressibility, $\lambda(\phi)$.

When a steady state is reached there will be a concentration profile (ϕ vs h) showing a constant concentration, ϕ, from the top to the height, h, where P_c is applied. From this point to the bottom a gradual increase should occur. An equation analogous to a first

order rate equation has been proposed.

$$\frac{D\phi}{Dt} = \lambda(\phi)\left[P(\phi) - P_c(\phi) \right]$$

$P_c(\phi)$ and $\lambda(\phi)$ can be measured by using a centrifuge to apply pressure to thicken the sediment while varying the starting concentration and the flocculant type and dosage. The parameters, $P_c(\phi)$ and $\lambda(\phi)$ can then be determined as functions of these control parameters and the action of the deep core thickeners optimized.

THE SURFACE CHEMISTRY OF LIGNITE

D.J. Readett

Following previous research aimed at understanding the process of surfacant assisted oil agglomeration and flotation of lignite, more work has been conducted in order to obtain a more detailed understanding of the surface chemistry of lignite.

The surface characteristics of Bowmans lignite were investigated using microelectrophoresis, standard salt titrations and potentiometric titrations. It was found that the determination of zeta potential was not an effective method of determining the lignite surface chemistry due to the complexity of the surface and the Stern region of the electrical double layer. For this reason, standard salt titrations were conducted to try and obtain some meaningful surface chemistry data. A series of potentiometric titrations was conducted which validated the salt titrations. The zpc of the

lignite was 3.6 in 10^{-1} M NaCl as electrolyte. Washing the lignite with sulphuric acid reduced the zpc slightly to 3.4. This is expected as it has been determined that acidic functional groups determine the surface characteristics of lignites. A model explaining the surface charging of lignite correlates favourably with the results obtained.

EXPERIMENTAL AND THEORETICAL ASPECTS OF THE SURFACE POTENTIAL OF IONIC MICELLES

Gregory V. Hartland

The surface potential of sodium dodecyl sulphate (SDS) micelles was measured by the apparent pK of an acid-base indicator, solubilized into the micelle. The indicator used was 4-heptadecyl -7-hydroxycoumarin. The surface potentials were measured under conditions of changing surface charge density and bulk ionic strength and the results analysed by a Gouy-Chapman-Stern model for the double layer of the micelle. The results indicate that the sodium counterions in the micelles' Stern layer bind between the sulphate head groups. When pentanol is solubilized by the micelle, the experimental potentials are smaller than predicted. The difference is attributed to an increase in the number of sites for counterion binding at the micelle surface.

RADIAL FLOW STREAMING POTENTIAL MEASUREMENTS ON FLAT PLATES

Peter Scales

The measurement of streaming potential is a well established method

of monitoring the zeta potential at the shear plane of non-colloidal particle masses and flat surfaces. The most common techniques rely upon flow of an electrolyte solution through a porous plug or capillary. This flow is responsible for movement of ions in the mobile portion of the electrical double layer. Under steady state conditions, a conduction current is set up to balance this movement. A steady state potential (streaming potential) may thus be measured and related to the zeta potential by the Smoluchowski equation.

The formation of a capillary as a separation between two flat plates allows the zeta potential of a number of different surfaces to be measured in a single apparatus. It also allows for the measurement of the zeta potential of coatings on these plates and ultimately the in situ measurement of shear plane and surface potential.

The successful measurement of streaming potential requires that a number of hydrodynamic and physical parameters are met within the design of the apparatus. The establishment of these parameters and initial experimental data on silica plates for a radial flow streaming potential apparatus will be presented.

THE CONDUCTIVITY OF DILUTE COLLOIDAL DISPERSIONS

D. Dunstan

The conductivity of colloidal systems is an area of considerable interest, the importance of such experimental studies lying in substantiating the fundamental electrostatic theories which govern colloidal phenomena.

To date, conductivity studies have been conducted on non-ideal systems where we believe both the presence of spurious surface groups and surface active impurities (from insufficient cleaning) have led to anomalous results. While the accurate experimental measurement of conductivity as a function of volume fraction, ϕ, is a non-trivial procedure (especially at high κa values), the accuracy is such that the disagreement with theoretically predicted conductivity cannot be ascribed to experimental error.

We have conducted studies on well characterized Polystyrene latex and Titanium dioxide, (TiO_2), dispersions. Both the TiO_2 and latices were stringently cleaned using an Amicon TCFIO ultrafiltration system. The suspensions were then filtered against a known electrolyte concentration to ensure that the filtrate has the same electrolyte concentration as the dispersion. The conductivities were then measured at 10kHz using an H-P 4192A Impedance Analyser.

In this paper we will present the suspension conductivity as a function of volume fraction of the suspension ($\phi < 0.5$) for different ζ- potential and κa systems. The experimental results are compraed with the theoretically predicted conductivites for these systems.

FLOTABILITY OF TAILORED QUARTZ PARTICLES

R.J. Crawford

Quartz particles have ben quantitatively methylated to varying known surface coverages by reaction with solutions of trimethylchlorosilane in cyclohexane in a dry environment. A pH difference technique was used to measure the uptake of trimethylchlorosilane. The flotation

behaviour of these quartz particles has been studied in a modified Hallimond tube. The effect of particle size, variation in concentration of electrolyte background and rate of flotation have been investigated.

Measurements of contact angles on quartz plates of varying hydrophobicity have also been performed and have been compared with those predicted by the Cassie equation.

A MONTE-CARLO STUDY OF ADSORPTION OF WATER VAPOUR ON QUARTZ

Anna Burgess

Pashley and Kitchener [J. Colloid Interface Sci., 71, 491-500, (1979)] published an experimental study of the adsorption of water on clean hydroxylated quartz. Near saturated vapour pressure the equilibrium water film thickness was much larger than expected. It is proposed to simulate the adsorption using a Monte-Carlo method with the aim of elucidating the experimental observations. A model for the water/quartz system will be discussed and preliminary results presented.

A METHOD OF CALCULATING THE SITE ENERGY DISTRIBUTION OF A HETEROGENEOUS SURFACE.

J. Lum Wan

A method of solution of the integral equation describing the relationship between the adsorption of gases onto a heterogeneous

surface and its site energy distribution is discussed. The theory is presented and techniques used in the numerical computation are described.

Simulated adsorption data (noisy and non-noisy) were used to recreate the site energy distribution using the DAIMEDNA series of algorithms, giving an idea of the accuracy of solution. The method provides solutions which are at best as good as the best methods produced thus far.

RHEOLOGY OF BROWN COAL SLURRY:- SURFACE CHEMISTRY ASPECTS

Y.K. Leong

The rheological characteristics of a concentrated Loy Yang brown coal (23% solid conc.) in terms of yield stress and apparent viscosity is explained by the electrophoretic mobility.

The yield stress and apparent viscosity were studied initially as a function of pH. They were high initially and dropped quite dramatically with pH. At a pH of about 4.0-5.0, the yield stress is non-existent and the apparent viscosity is at its minimum. To explain such rheological behaviour, the electrophoretic mobility is measured as a function of pH. The significance of the mobility parameter is that it tells us the nature of interaction between the particles. A low absolute value of the mobility, means that the net interaction between the particles is attractive and the slurry is therefore strongly flocculated. Conversely, a high absolute mobility value, implies that the net particle interaction is repulsive and the slurry is well dispersed. The rheological characteristics of the

slurry were found to be consistent with the electrophoretic mobility result. The slurry with high yield stress and high apparent viscosity was found to correspond to low mobility values. As the yield stress and apparent viscosity decreased, the particle mobility was found to increase correspondingly.

The rheological flow curves of a flocculated brown coal slurry (low mobility value) and a well-dispersed slurry (high mobility value) were also illustrated. A well-dispersed slurry showed Newtonian rheological behaviour and a low viscosity. The flocculated slurry showed yield stress behaviour and is also characterised by high viscosity.

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

Calum Drummond

Acid-base indicators are increasingly being used as probes of the interfacial microenvironment of micelles, microemulsions, vesicles and biological membranes. When an acid-base indicator is solubilized in one of the above systems the acid-base equilibrium (i.e. the pK_a value) of the indicator is shifted. In order to help clarify the reasons for this apparent pK_a change when an acid-base indicator resides at an uncharged interface we have performed pH titrations with a wide range of acid-base indicators in a number of organic solvent/water mixtures and in several nonionic micelles. The results of these experiments will be presented and the nature of the interfacial microenvironment of nonionic micelles discussed.

LASER DOPPLER ELECTROPHORESIS (LDE)

David Hayes

Light scattered from moving objects has its frequency Doppler shifted. The recent development of laser beat spectroscopy has enabled these small frequency shifts to be measured. The application of this technique to the measurement of electrophoretic mobilities has the potential to determine mobility values rapidly and objectively even with heterogeneous systems. The method used to obtain mobility values with laser beat spectroscopy will be described and problems inherent in the technique will be discussed and compared with other techniques. Application of LDE to systems of cells, macromolecules and colloids will be briefly reviewed and preliminary results obtained with our own apparatus will be presented.

ATTENUATED TOTAL REFLECTANCE (ATR) STUDIES OF MODEL SOLID-AQUEOUS INTERFACES

Janine Godfrey

The ATR technique can be used to sample the interfacial environment of a long chain ionizable chromophore embedded in a Langmuir-Blodgett cast film. The monomolecular film, composed of the probe and a lipid diluent is deposited, in the usual manner, onto a transparent solid which is used as the multiple internal reflection element. The degree of ionization, α, of the chromophore can be obtained spectroscopically as a function of pH. By using simple Gouy-Chapman theory, α vs pH and pK_{app} vs pH plots can be obtained.

Experiments to date have shown an unusual but reproducible minimum in the plot of pK_{app} vs α in the low charge region. A model is discussed which requires charge dependent orientation of water dipoles at the interface. Preliminary experiments which will further investigate this behaviour are discussed.

SOME ASPECTS OF PROTOTROPIC REACTIONS AT INTERFACES
Matt Lay

A kinetic approach to surface chemical problems is often profitable. Some methods for a kinetic study of surface ionization will be presented. These involve the use of ionizable, fluorescent probes.

Preliminary results indicate that changes in water-structure at aqueous interfaces, for example those in microemulsions, have a substantial effect on the rate of ionization.

THE PARTITIONING OF POLYDISPERSE NON-IONIC SURFACTANTS BETWEEN OIL AND WATER
Gregory C. Allan

The partitioning of a polydisperse non-ionic surfactant, nonyl phenol polyoxyethylene with an average of 7.3 ethylene oxide units $(CH_3(CH_2)_8 - C_6H_6 - (OCH_2CH_2)_{7.3} - OH)$, between water and a second, immiscible oil (hexane) phase has been investigated. The surfactant has been well characterized by U.V. absorption, surface tension, cloud point measurements, and gas chromatography.

The total partitioning of the surfactant between the two

immiscible phases has been studied as a function of temperature, allowing calculation of the standard free energy, enthalpy, and entropy of phase transfer of 1 mole of surfactant, which were determined to be 22 ± 5 kJ/mol for ΔH° and 85 ± 16 J K^{-1} mol^{-1} for ΔS°.

The partitioning of the surfactant between oil and water has been further studied by investigating the partitioning of individual components of the polydisperse surfactant using gas chromatography. The change in distribution of the components in both phases was measured as a function of total surfactant concentration, and compared to a phase separation model of aqueous micelles, developed elsewhere, which describes partitioning behaviour of mixed systems.

Standard free energies of transfer between oil and water were measured for each component of the surfactant distribution as a function of temperature. This allowed calculation of the standard free energy of phase transfer as a function of ethylene oxide chain length, at each temperature. An unsuccessful attempt was also made to calculate standard entropies and enthalpies of phase transfer of each component of the surfactant distribution.

ADSORPTION OF ORGANIC MOLECULES AT THE SOLID/AQUEOUS INTERFACE
Robert Sheers

The determination of zeta-potential by radial flow streaming potential measurements on flat plates and UV Attenuated Total Reflectance (ATR) spectroscopy are two methods to be used to obtain thermodynamic data relating to adsorption from solution.

The particular advantages of applying these methods to obtain qualitative and quantitative data are described.