

ELEVENTH

AUSTRALIAN COLLOID AND SURFACE CHEMISTRY

STUDENT CONFERENCE

UNIVERSITY OF SYDNEY

(YARRAWOOD)

1983



PROCEEDINGS AND ABSTRACTS
 OF THE ELEVENTH
 AUSTRALIAN COLLOID AND SURFACE CHEMISTRY
 STUDENT CONFERENCE
 UNIVERSITY OF SYDNEY, 1983

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ACKNOWLEDGEMENTS

Students and University staff, CSIRO and industry participants contributed financially to the running of the Conference. Major financial support was provided by the University of Melbourne, by I.C.I. (Australia), and by Dulux Australia. Contributions were also received from the Australian National University, Unilever (Australia); Catoleum and Dispensers Pty. Limited. Because it normally provides only limited travelling allowances for conference participants, the University of Sydney was unable to make any contribution on this occasion.

All concerned with the meeting thank those sponsors for making this and other Australian Colloid Student Conferences possible. The participants also wish to thank their Sydney hosts and especially the Conference organisers: Dr Don Napper and Mr Matt Ballard for their efforts in making the meeting a success.

Special Note

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

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University of Sydney
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or

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Department of Physical Chemistry
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Cover:

Freeze Fracture Photograph of Swollen Latex Particles
(20 000 X approx.)

PREFACE

The Eleventh Australian Colloid and Surface Chemistry Student Conference was held at the Yarrowood Conference Centre just outside Sydney in May 1983. The abstracts which follow were prepared by the postgraduate students from the Universities of Melbourne, Sydney, ANU, NSW, Monash and from RMIT and Swinburne Institute of Technology.

As at previous student conferences, all papers were presented by the postgraduate students to an audience of their peers, their immediate supervisors and other local scientists from Australian Government and industrial research centres. We also were pleased to have with us Dr Richard Buscall of ICI (Runcorn, U.K.) who took an active part in the proceedings. The papers continued the general high standard of content and presentation which we have come to expect.

The Conference served also to bring together the participants in the production of a major treatise on Colloid Science which is presently in preparation. This book, affectionately known as "Colloid Oz", is in many respects an outgrowth of the Student Conferences because they have served to generate and maintain the cohesive character of Australian colloid science and to assist us all to a more global view of our chosen area of professional expertise. If we can capture in that text even a fraction of the spirit of active scientific enquiry and creative teaching which epitomises the Student Conferences then the effort involved will no doubt be regarded as worthwhile by all those involved.

Because of an unusual combination of circumstances we departed from our usual procedure of calling on one of our senior graduate students

to act as Conference Secretary. It is a pleasure to record our debt of gratitude to Don Napper for taking on that task and carrying it through with such skill and apparent ease, despite his many other commitments (including Headship of the School of Chemistry). With such enthusiastic support available it is obvious that the Colloid Student Conference has a bright future whatever befalls the old timers like me.

Bob Hunter,
Sydney 1983.

PARTICIPANTS - 1983

Guest of Honour

Dr Richard Buscall (I.C.I., Runcorn)

From the University of SydneyStaff

Associate Professor R.J. Hunter
 Associate Professor D.H. Napper
 Dr R.G. Gilbert

Students

M. Ballard
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 M. Adams
 N. Ekdawi
 J. Feeney
 B. MewJork
 D. Arthur
 M. Hammond
 R. Vegners
 L. Halnan
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 B. Whang

From the University of MelbourneStaff

Professor T.W. Healy
 Dr Lee White
 Dr F. Grieser

Students

R. Lamb
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 J. Godfrey
 M. Gee
 A. Burgess
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 A. Lau
 I. Metcalfe
 J. Aston
 J. Lum Wah

From the Australian National UniversityStaff

Dr D. Chan
 Dr R. Pashley

Students

B. Beresford-Smith
 L. Angel

From the University of New South WalesStaff

Professor C. Fell
 Dr A. Frayne
 Dr R. O'Brien

Students

R. McDonogh
 S. Puttock
 B. Yoo

From Monash University

R. Mills (student)

From Royal Melbourne Institute of Technology

P. Daivis (student)

From Swinburne Institute of TechnologyStaff

Dr J. Ralston
 Dr D. Atkinson

Students

V. Nyman

From CSIRO (Applied Organic Chemistry)

Dr N. Furlong

From I.C.I. (A.N.Z.)

Dr G. Halliday
 Dr S. Margetson
 Mr J. Lyons

From Dulux (Australia)

Mr L. Rowe

ELEVENTH AUSTRALIAN COLLOID STUDENT CONFERENCE

MAY 1983, YARRAWOOD NSW

PROGRAMME

Opening Session

Thursday, May 19

School of Chemistry, University of Sydney

9.00 am - 1.00 pm
12.30 pm - 2.00 pm

Registration
LUNCH (University Staff Club)

Chairman: Associate Professor Bob Hunter

2.00 pm - 2.30 pm
2.30 pm - 3.00 pm
3.00 pm - 3.30 pm
3.30 pm - 4.00 pm
4.15 pm
7.00 pm

Greg Warr, University of Melbourne
"On the Measurement of Micelle Size Distributions"
John Feeney, The University of Sydney
"Coagulation vs Micellar Entry in Latex Particle Nucleation"
Robert Lamb, University of Melbourne
"New Method of Simultaneous Measurement of Contact Angle and Surface Tension"
Bruce MewJork, University of Sydney
"Electrical Conductivity of Colloidal Dispersions"
BUS TO YARRAWOOD
DINNER

Friday, May 20

Yarrawood Centre

Chairman: Professor Tom Healy

9.00 am - 9.30 am
9.30 am - 10.00 am
10.00 am - 10.30 am
10.30 am - 11.00 am

Bryan Beresford-Smith, ANU
"The Effective Pair Potential for Strongly Interacting Colloidal Systems"
Nagi Ekdawi, University of Sydney
"The Sedimentation of Dispersed and Coagulated Dispersions at High Volume Fractions"
David Dunstan, University of Melbourne
"Capillary Rise in Porous Media"
COFFEE

Chairman: Dr Lee White

- 11.00 am - 11.30 am Simon Puttock and Ben Yoo, UNSW
 "Surface Phenomena in the Filtration and Dewatering of Alumina"
- 11.30 am - 12.00 noon Jeff Aston, University of Melbourne
 "The Significance of Plateau Adsorption"
- 12.00 pm - 12.30 pm Matt Ballard, University of Sydney
 "Emulsion Polymerization of Methyl Methacrylate"
- LUNCH*
- 1.30 pm - 3.45 pm *Staff-Student Cricket Match*

Chairman: Associate Professor Don Napper

- 4.00 pm - 4.20 pm Janine Godfrey, University of Melbourne
 (Hons.) "Electrokinetic Studies of Adsorbed Surfactant Monolayers"
- 4.20 pm - 4.40 pm David Arthur, University of Sydney
 (Hons.) "Rheology of a Montmorillonite Dispersion"
- 4.40 pm - 5.00 pm Michelle Gee, University of Melbourne
 (Hons.) "Light Scattering from Polystyrene Latex Dispersions"
- 5.00 pm - 5.20 pm Michael Hammond, University of Sydney
 (Hons.) "The Effects of Polymeric Surfactants on the Growth of Polystyrene Latex Particles"
- 6.30 pm *BARBEQUE*

Saturday, May 21Yarrawood CentreChairman: Dr John Ralston

- 9.00 am - 9.30 am Veronika Nyman, SWIT
 "Potentiometric Titrations of Lignins"
- 9.30 am - 10.00 am Russel Mills, Monash University
 "Polymeric Flow Improvers"
- 10.00 am - 10.30 am Peter Davis, RMIT
 "Dynamic Light Scattering from Polymer Solutions"
- 10.30 am - 11.00 am *COFFEE*

Chairman: Dr Richard Pashley

- 11.00 am - 11.30 am Anna Burgess, University of Melbourne
 "Theoretical Considerations of the Adhesion of Smooth Surfaces"

- 11.30 am - 12.00 noon Ray Vegners, University of Sydney
"Preparation of Solar Selective Coatings"
- 12.00 pm - 12.30 pm Ian Penboss, University of Sydney
"The Entry of Free Radicals into Latex Particles"
- LUNCH*
- 2.00 pm - 2.30 pm Anthony Chetcuti, University of Sydney
"Chemical Aspects of the Preparation of SYNROC"
- 2.30 pm - 3.00 pm Alice Lau, University of Melbourne
"Adsorption of Uranyl Ions on Various Substrates"
- 3.00 pm - 3.30 pm Lindsay Angel, ANU
"Fundamental Studies of 3-Component Microemulsions"
- 3.30 pm - 4.00 pm *COFFEE*

Chairman: Dr Neil Furlong

- 4.00 pm - 4.30 pm David Hayes, University of Melbourne
"Monolayer Studies of Octadecyloxynaphthoic acid"
- 4.30 pm - 5.00 pm Mary Adams, University of Sydney
"MWDs as a Probe of Latex Nucleation Processes"
- 5.00 pm - 5.20 pm Robert Hayes, University of Melbourne
(Hons.) "The Photocatalytic Production of H₂ and O₂ from Water on Doped CdS Colloids"
- 5.20 pm - 5.40 pm Leslie Halnan, University of Sydney
(Hons.) "Growth of Poly(butylmethacrylate) Latex Particles"
- 7.00 pm *CONFERENCE DINNER*

Sunday, May 22 Yarrawood Centre

Chairman: Professor Tom Healy

- 9.15 am - 9.45 am R. McDonogh, UNSW
"Surface Phenomena in the Ultrafiltration of Colloids"
- 9.45 am - 10.15 am Ian Metcalfe, University of Melbourne
"A New Approach to Site Energy Distribution"
- 10.15 am - 11.00 am Dr R. Pashley, ANU
"Recent Developments in the Direct Measurement of Surface Forces"
- LUNCH*
- 2.00 pm *BUSS TO AIRPORT/UNIVERSITY OF SYDNEY*

ABSTRACTS

The Size Distribution of Micelles of Nonionic Surfactants

Greg Warr (Melbourne)

Two experimental methods for studying the size distribution of nonionic surfactant molecules are presented. The first, a fluorescent probe quenching technique, has been used in computer simulation studies to determine with a high degree of accuracy the first three moments of model distributions. An evaluation of the experimental parameters governing this technique is discussed in light of the results of the simulation.

Secondly, the results of a novel ultrafiltration study of the size distribution of micelles of a polyoxyethylene nonylphenol are given as a function of concentration (from one to twenty times the cmc). From these experiments, micelle size distribution histograms have been constructed, and weight-average micellar molecular weights determined. These averages are in very good agreement with the results of a light scattering study of solutions of the same surfactant.

Coagulation vs. Micellar Entry in Latex Particle Nucleation

John Feeney (Sydney)

The mechanism by which latex particles are created in an emulsion polymerization will influence such properties of the latex as particle number and their size distribution.

Particles are nucleated (or created) with a very small radius (at least less than 5 nm) so are not observable by conventional electron microscopy. However, if they are allowed to "grow" to a larger volume before sampling, the particle size distribution (PSD) still reflects the nucleation mechanism.

Three mechanisms have been postulated: the two single step mechanisms of homogeneous and micellar entry and the two step mechanism of precursor nucleation with subsequent coagulation to form latex particles. One may differentiate between the single step and double step mechanisms by their respective rates of nucleation.

The rate of nucleation will effect the PSD, particularly the sign of the skewness. Thus by measuring an experimental PSD and comparing it with a theoretical solution to modified Smith-Ewart equations incorporating the rate of nucleation, the nucleation mechanism may be derived.

In the emulsion polymerization systems of styrene so far studied, the two step mechanism was found to be dominant.

Interfacial Tension and Contact Angles from Sessile and Pendant Drops

Rob Lamb (Melbourne)

A simultaneous method for the determination of liquid surface tension and contact angle from drop profiles was described. Numerical integration of the equations to describe the profile produces theoretical curve shapes of known surface tension and size. A non linear regression technique was used to fit these curves to experimental shapes by optimizing size, liquid tension and magnitude of 2-co-ordinates. Once satisfactory fit is obtained integration to the baseline of the shape produces a contact angle value. The error in this method is associated purely with calculation of surface tension. Non-assymetry or the onset of profile sphericity reduces accuracy but is assessed by reference to measurement of computer simulated profiles. Contact angles are a geometrical feature only. Correct scaling of the magnified drop profile was found to be essential however to any surface tension analysis.

Comparison of tension measurements with those of experimental capillary rise results were shown to be in agreement to the first decimal place for liquid tensions less than 100 mN/m. Contact angles were correct to one degree throughout all tension and size ranges.

The Electrical Conductivity of Dilute Suspensions of Polystyrene

Bruce MewJork (Sydney)

The systems being used in this work are dilute monodisperse polystyrene dispersions. The conductance of suspensions is of interest in the confirmation of the assumptions used in electrokinetic theory. The particles have been shown to have a radius of 50 nm and to be spherical from electron microscopy. Potentiometric titrations have been used to estimate the surface charge per unit area. A modified cleaning procedure combining

ultracentrifugation and ultrafiltration techniques has been employed to ensure a clean particle surface. Pulsed proton N.M.R. has been used in conjunction with this process in an attempt to detect any surface-associated polymeric contaminants that could possibly contribute to an unwanted "rough" surface. To date the N.M.R. experiments have been unsuccessful. A new method of determining the value K^{∞} (the conductivity of the bathing electrolyte) has been proposed by equilibrating the ultrafiltrate with the particles during the cleaning process.

The Effective Pair Potential for Strongly Interacting Colloidal Dispersions
Bryan Beresford-Smith (ANU)

In the classical DLVO theory of electrical double layer interactions the exponential screening length of the pair interactions is determined by the known properties of an infinite reservoir which is in osmotic equilibrium with the colloidal dispersion. Often in practice no such reservoir exists and the colloidal particles, together with their dissociated counterions and any added electrolyte, form an isolated system. What then is the double layer interaction?

In this paper we introduce a so-called Jellium Model to answer this question. The appropriate screening length for the pair potential then turns out to be dependent on the density of the colloidal particles and the amount of added salt [1].

The predictions of the theory are compared with the structure factor for aqueous dispersions of charged polystyrene spheres as measured by light and neutron scattering techniques [2].

References

- [1] B. Beresford-Smith and D.Y.C. Chan, 1982, Chem. Phys. Lett. 92, 474;
B. Beresford-Smith and D.Y.C. Chan, 1983, Disc. Farad. Soc., 76.
- [2] J.C. Brown, P.N. Pusey, J.W. Goodwin and R.H. Ottewill, 1975, J. Phys. A 8, 664;
R.H. Ottewill, 1982, in Spec. Publ. - R. Soc. Chem., 43.

Sedimentation of Disperse and Coagulated Suspensions at High Volume Fractions
Nagi Ekdawi (Sydney)

The sedimentation process of concentrated suspensions has always been important in industry. However due to the complex interactions between particles at high volume fractions, this phenomenon was never modelled.

By a few simple assumptions (namely that the velocity of sedimentation is solely determined by the local particle concentration which affects both the local apparent density (ρ_s) and viscosity (η_s) of the suspension), we were able to develop a model explaining the sedimentation behaviour of dispersed suspensions (concentrated).

Furthermore, we looked at the sedimentation behaviour of coagulated suspensions of large particles ($> 5 \mu\text{m}$) (which have negligible colloidal forces acting between them with respect to other forces) and we developed a model which assumes that the settling flow units are individual particles settling in the same manner as the dispersed concentrated suspensions. However for flocculated suspensions we had to take account of interparticle interactions, restricting the fluid flow to some extent. Consequently we introduced a parameter (β) which indicates the degree to which the true particle volume fraction is effectively augmented by the restriction of the fluid flow. This model was tested using experimental data from Steinour, and Obiakor and Whitmore, and it was found to work very well at particle volume fractions above 20 %.

Capillary Rise in Porous Media

David Dunstan (Melbourne)

An experimental study of capillary rise in porous media has been conducted using packed beds of glass spheres. The purpose of the study is to evaluate White's (J. Colloid & Int. Sci. 1982) thermodynamic theory relating the observed pressure difference in the bed to (i) the effective capillary radius of the packed bed, (ii) the contact angle.

Good agreement between theory and experiment is observed for the contact angle data. Reasonable but not as good agreement is found for the variation of effective capillary radius with observed pressures.

*Surface Phenomena in the Filtration and Dewatering of Alumina*Simon Puttock and Ben Yoo (NSW)

The production of alumina *via* the Bayer process is of major importance for the Australian mineral industry. One specific stage of this process involves the filtration and subsequent dewatering of precipitated alumina trihydrate, in which the residual moisture content of the filter cake is significantly reduced.

It is anticipated that a detailed study of the factors which influence this dewatering process will lead to improved cake drainage characteristics and hence a drier filter cake.

Our initial investigations have been to study the role of particle parameters on filter cake dewatering characteristics, and to effect improved dewatering with the use of surfactants. The overall objective will be to provide firstly, a formal basis for the choice of surfactant in terms of its surface wetting and adsorption properties, and secondly a detailed understanding of the location of residual water within a typical filter cake.

*Adsorption Density at the Isotherm Plateau*Jeff Aston (Melbourne)

Adsorption studies at the solid/solution interface for a short chain alcohol 2 hydroxyl-4-methyl pentanol (MIBC) and a polyoxyethylene nonyl phenol (N9) revealed information on the nature and size of the porosity of coal.

MIBC adsorption gave very high adsorption densities with equilibrium occurring after 60 - 100 hours. The area/molecule of 2 \AA^2 for MIBC was taken as evidence for the inapplicability of the N_2 adsorption B.E.T. surface area for coal when considering the adsorption of small molecules from aqueous solution.

Surface tension and pressure/area studies at the air/water interface showed the close packed area/molecule for a monolayer of MIBC to be 38 \AA^2 /molecule compared with $\sim 25 - 29 \text{ \AA}^2$ /molecule for a straight chain alcohol. Assuming this area/molecule to be applicable to the formation of a monolayer at the solid/liquid interface which is supported by

adsorption and contact angle studies of MIBC on non-porous silica and methylated silica the expected surface area of the coal is $\sim 70 \text{ m}^2/\text{g}$.

N9 gave an adsorption density on coal in agreement with that for the non-porous silica and methylated silica i.e. $\sim 60 \text{ \AA}^2/\text{molecule}$. Pore size distribution studies illustrate the microporous nature of coal.

The Emulsion Polymerization of Methyl Methacrylate

Matt Ballard (Sydney)

Many workers have studied the emulsion polymerization of methyl methacrylate and noted the sigmoidal shape of the conversion curve. However, they failed to note that monomer droplets are present well in the region of non-steady-state rate of reaction. In a thorough study of seeded (37 and 47 nm particles) systems, it was found that the rate of reaction increases linearly with time (t) or conversion (x) whilst monomer droplets are present; i.e.: during stage II. The magnitude of this increase in rate is 50-100%. This means that the traditional means of determining the rate coefficients ρ , k and c from the steady-state value of \bar{n} are in fact incorrect, as there is no steady-state.

Close inspection of the rate versus conversion curves showed that \bar{n} varied linearly with conversion:

$$\bar{n} = \bar{n}_0 + \bar{n}_1 x$$

and that the quantity \bar{n}_1/\bar{n}_0 was independent of initiator concentration, surfactant type, surfactant concentration and seed latex. Within the Smith-Ewart framework, the only model that predicts an \bar{n}_1/\bar{n}_0 independent of these variables is one with:

$$\begin{aligned} \alpha \text{ (re-entry parameter)} &= +1 \\ k &\geq c \\ c &= c_0 + c_1 x \end{aligned}$$

Further, if the change in c with conversion is ascribed to the increase in particle volume with conversion:

$$c = k_t/N_A V = c_0 \left(1 + \frac{x}{p_0}\right)$$

then the predicted value of $\bar{n}_1/\bar{n}_0 = 1/2p_0$, where p_0 is the initial amount of polymer.

*Electrokinetic Studies of Adsorbed Surfactant Monolayers*Janine Godfrey (Melbourne)

The measurement of the electrokinetic properties of ionisable surfaces prepared as cast films, using a radial flow streaming potential apparatus will complement current spectroscopic measurements of the surface potential, using silica plates.

The classical Langmuir-Blodgett technique is used to cast the monolayers which consist of a chromophore and a lipid diluent. Electron Diffraction has revealed that the cast film has a highly ordered structure, resulting in a well characterised and reliable surface with which to work.

Thus, the zeta potential and the total double layer potential of a surface, which are usually only related by models will be directly measurable.

*Rheology of Montmorillonite Suspensions*David Arthur (Sydney)

Rheological and colloidal properties of the clay mineral montmorillonite, in suspension are of commercial significance due to their use as bentonite suspensions for drilling muds in the oil industry. Since these properties are manifestations of particle interactions, the aim of the work is to examine these interactions by rheological investigation.

A brief description of the constant stress rheometer was given, as was a description of the flow curves (stress-shear relations) that are anticipated.

The essential features of the system to be studied, namely the suspension of negatively charged platelets with strong van der Waal's forces between them, was outlined, along with a brief discussion of the origin of some of these.

The particle interactions are to be investigated by varying properties of the medium, namely the pH and the electrolyte concentration, and examining the effect this has on the system's rheological response.

Light Scattering Studies on Polystyrene Latices

Michelle Gee (Melbourne)

The project will involve the preparation of very small monodispersed polystyrene latices stabilised by sulfate surface groups. Ultrafiltration and dialysis techniques are employed in the purification of the latex dispersions.

Time resolved light scattering experiments will be performed at low latex concentrations in the hope of obtaining information on the pair potential and radial distribution function of latex sols as a function of electrolyte concentration and to determine the effect, if any, of the method of purification on the repulsion and consequently the short range structure of the dispersions.

The Effects of Polymeric Surfactants on the Growth of Polystyrene Latex Particles

Michael Hammond (Sydney)

The industrial polymerization of styrene is carried out using polymeric surfactants such as PVOH in order to stabilize the growing latex particle. As yet, very little research has been done in this area in order to understand the effects of such surfactants, as opposed to using short chain organic surfactants such as SDS or POL.

Polymeric surfactants are typically graft copolymers containing the soluble stabilizing moiety as the backbone (e.g. PVOH) with an insoluble anchor (e.g. styrene) grafted on to attach it securely to the latex particle. A stabilizer is needed to prevent coagulation during the polymerization. One problem which is encountered in the preparation of the copolymer is that a fine balance must be achieved between the amount of stabilizer and the amount of anchor, so that the surfactant will still be soluble, but be an efficient anchor at the same time. To determine if the surfactant is anchored sufficiently to the latex, a flocculation experiment is carried out to determine at what temperature the coated latex flocculates. If sufficiently anchored, flocculation occurs at the c.f.pt. of the stabilizing moiety.

Results obtained for entry and exit coefficients of free radicals will be compared with those already known for polymerization using SDS as the surfactant, and from the difference, the effect of the polymeric surfactant on the rate will be determined and a mechanism modelled.

PVOH = polyvinylalcohol

SDS = sodium dodecyl sulfate

POL = potassium oleate

Potentiometric Titration of Lignins

Veronika Nyman (Swinburne)

Lignin is a naturally occurring macromolecule, which provides structural support in plants. During the process of wood pulping its structure is significantly altered, the important changes being the introduction of acidic groups into the molecule.

Pure lignin samples have been obtained from the liquors resulting from Kraft and NSSC wood cooks. A variety of solution studies have been made with these lignins, in particular, potentiometric titrations. Equivalence points and thus values for α' , the degree of neutralisation, have been derived. Henderson Hasselbach plots have been applied unsuccessfully, to provide information on lignin structural changes. Finally, a thermodynamic method of analysis which involves the determination of the intrinsic dissociation constant, pK_0 , has been used.

Polymeric Flow Improvers

Russell Mills (Monash)

The commercial exploitation of crude oils and their derived products having high wax contents is limited by handling problems which arise at low temperatures. Such problems include increased yield stresses, non-Newtonian flow behaviour, poor "pumpability" and filter blockages resulting from separation of the wax from solution.

Additives have been developed to overcome this problem by modifying the crystal habit of the waxes and by delaying their nucleation. A particularly effective additive has been used in distillate fuels containing high n-paraffin wax contents. This is the ethylene-vinyl acetate copolymer.

Structural studies are now being undertaken to establish the role of the copolymer structure in its effectiveness and as a nucleation retarder. The techniques being used are Size Exclusion Chromatography for molecular weight distributions and ^{13}C n.m.r. for sequence distribution.

Some copolymers have been prepared by free-radical addition copolymerization in solution and a couple have been shown to be particularly effective at delaying the nucleation of $n\text{C}_{36}\text{H}_{74}$ in O-Xylene solutions. The relationship between the synthesis conditions, copolymer characteristics and their effectiveness is discussed and a mechanism of incorporation of copolymer molecules into the n-paraffin crystal is proposed.

Dynamic Light Scattering from Ternary Polymer-Polymer-Solvent Systems
Peter Daivis (RMIT)

The results of dynamic light scattering experiments on solutions containing approximately 5 kg m^{-3} of dextran polymer with $M_w = 8 \times 10^5$ and concentrations ranging up to approximately 150 kg m^{-3} of dextran with $M_w = 2 \times 10^4$ are presented. They are interpreted using theory due to Pusey, Fijnaut and Vrij [1] to obtain diffusion coefficients for two independent modes of relaxation of concentration fluctuations. These diffusion coefficients are used to obtain the product of the more commonly used cross diffusion coefficients as a function of the concentration of the low molecular weight solute.

[1] P.N. Pusey, H.M. Fijnaut and A. Vrij, *J. Chem. Phys.*, 77, 4270, (1982).

A Physically Consistent Theory of Adhesive Contact of Elastic Solids
Anna Burgess (Melbourne)

There has been much debate in recent years concerning the validity of various adhesive theories. The main problems with the contending theories were briefly discussed. A new theory proposed by Hughes and White was then presented, and shown to be physically sensible.

Results from numerical solution of the Hughes-White equations were then used to indicate the manner in which adhesive contact behaviour depends on the elastic constants of the contacting bodies, on the surface energies of the bodies and on the range of the van der Waals forces of

the surfaces of the bodies. The excellent agreement with experimental results was noted.

Preparation of Spectrally Selective Surfaces for the Photothermal Conversion of Solar Energy

Ray Vegners (Sydney)

Materials called cermets (transition metal particles or layers inside a semi-conductor host) have been shown to exhibit the properties required for the efficient conversion of solar energy for heating purposes. This "efficiency" is due to the absorption of solar flux at wavelengths below 2000 nm and reflectance above 2000 nm, hence yielding a surface that can produce temperatures of around 300 °C, where these temperatures are much higher than those obtained by simple black surfaces (i.e. black body radiators).

The method proposed in producing cermet surfaces utilises a patented invention by R.K. Iler [1] in which the deposition of several oppositely charged monolayers [2] of the transition metal and of the semi-conductor upon a substrate [3] yields the required surface for solar collectors.

It is hoped that by using copper and silica sols absorptions greater than 90% of the incident solar flux with emissions less than 5% will be obtained.

- [1] Iler, R.K. Patent No. 3 485 658. U.S. Patent Office (1969).
- [2] The deposition of these monolayers occurs by the immersion of the charged surface into a dilute monodisperse colloidal sol of opposite charge. After rinsing, the resulting surface is ready for immersion into another oppositely charged colloidal sol.
- [3] The substrate is typically a transition metal layer on a glass (or plastic (if possible)) surface that conducts the thermal energy to the medium being heated.

The Entry of Free Radicals into Polystyrene Latex Particles

Ian Penboss (Sydney)

The results were reported of a series of kinetic studies of the seeded emulsion polymerization of styrene designed to investigate the

effect of different initiator species on the rate coefficient for the entry of free radicals into the latex particles. The initiators employed were persulfate anions, neutral hydroxyl free radicals and 2,2'-azobis-(2-amidinopropane) hydrochloride (generating positively charged free radical species).

Entry rate coefficients were determined from the observed rates of approach to the steady state, making due allowance for the processes of free radical exit, re-entry and aqueous phase heterotermination.

The dependence of the entry rate coefficient (ρ_I) on particle number density (N_C) and initiator concentration $[I]$ was fitted by a mechanism incorporating the conversion of initiating free radical species into oligomeric free radicals, mutual aqueous phase termination of these oligomers, and entry of these oligomers into latex particles. This gives an expression for $\rho_I(N_C, [I])$ containing only two rate parameters (B and γ):

$$\rho_I = \gamma \left\{ \left[(N_C^2/N_A^2) + 4B[I] \right]^{1/2} - (N_C/N_A) \right\}$$

where N_A is Avogadro's number.

It was found that data over wide ranges of $[I]$ and N_C could be accurately fitted with this expression. It was thus found that the charge on the initiating species has only a weak effect on the entry and mutual termination of oligomeric free radicals, indicating that both processes are dominated by the hydrophobic tail of the species involved.

The Synthesis of Ceramic Powders using Metal Alkoxides

A. Chetcuti (Sydney)

Highly reactive powders are desirable for many chemical and physical processes (ion-exchange, adsorption, chemisorption, sintering, etc.). The production of fine, chemically homogeneous and highly reactive material is desirable where the synthesis and fabrication of multicomponent ceramic systems such as *synroc* are concerned. *Synroc* powder is a matrix consisting of Al_2O_3 , BaO , CaO , TiO_2 and ZrO_2 , which, when fabricated at a pressure of 14 MPa and a temperature of 1150 °C results in the formation of the crystalline titanate based ceramic. *Synroc* (acronym meaning synthetic rock) will ultimately be utilised for the fixation of high level liquid waste generated from nuclear power reactor operation.

Metal alkoxide hydrolysis coupled with ion-exchange has been successfully used to produce a good sinterable *synroc* product.

Surface area and x-ray diffraction data for both ball-milled metal oxide and alkoxide-derived material are compared. The results clearly show an increased powder reactivity and lower process temperature requirements for the powder synthesised via metal alkoxide decomposition.

Uranium(VI) Species at Solid-Aqueous Interfaces - Electrokinetic and Adsorption Studies

Alice Lau (Melbourne)

In acidic solutions, uranium(VI) exists as hydrated uranyl ion (UO_2^{2+}). It is readily hydrolysed to give mononuclear and polynuclear species such as $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$.

The behaviour of uranium(VI) species on titanium dioxide, silica and carbon black surfaces was studied, as a function of pH, using electrokinetic and adsorption techniques.

Results from electrokinetic studies suggest that uranium(VI) species specifically adsorbed at surfaces of various substrates; inducing an increase in their respective isoelectric points. Adsorption phenomena were found to be significantly different among the three types of substrates, with uranyl ions shown to be the adsorbing species onto titanium dioxide surfaces. The adsorption of uranium(VI) onto silica and carbon black was complicated by the hydrolysis products of these uranyl ions. However, all three substrates do exhibit similar values for the maximum number of adsorbing species per unit area of substrate.

Studies on Three-Component Microemulsions

Lindsay Angel (ANU)

The surfactant didodecyldimethylammonium bromide [$(\text{C}_{12}\text{H}_{25})_2\text{N}(\text{CH}_3)_2\text{Br}$] has been shown to form water in oil microemulsions without the aid of any co-surfactant. Water to surfactant mole ratios in excess of 140 have been attained in some cases, with the system remaining clear and freely flowing.

Three component water/surfactant/oil phase diagrams for the hexane, octane, decane and dodecane systems are presented and discussed. Preliminary conductivity data for the microemulsion phase is discussed in terms of the equation deduced by Eicke and Denss for the Aerosol OT/Water/Benzene system.

Monolayer Studies of Octadecyloxynaphthoic Acid

David Hayes (Melbourne)

The functional surfactant octadecyloxynaphthoic acid (ONA) has been studied at the air/water interface using classical surface pressure-area (π -A) measurements and surface fluorescence techniques.

The π -A studies on 10^{-1} M KNO_3 subphase indicated that multilayers of DNA formed at the interface below pH 8.0 indicating a strong aggregating force between neutral ONA molecules. Above pH 8.0 monolayers were obtained as ONA was ionised at the interface. A monolayer of neutral ONA was obtained when the pH was reduced beneath a monolayer of ionised surfactant. The effect of ionisation on the π -A isotherm was thus obtained and analysed using the theory of Davies. This analysis showed aggregation forces were decreasing the surface pressure of the ionised monolayer.

Surface fluorescence techniques were used to follow the ionisation reaction at the air/water interface. The results indicated an effective pK_a of 9.5 for ONA at the interface. This result could be correlated with the π -A isotherms observed.

Molecular Weight Distributions as a Probe of Latex Nucleation Processes

Mary Adams (Sydney)

The mechanisms involved in particle nucleation in an emulsion polymerization reaction have long been a topic of debate. In recent times the work of the Polymer Group at the University of Sydney has provided a reasonably clear explanation of the kinetic processes involved in polymer latex particle growth in seeded emulsion polymerization systems. However, to date, there has been little investigation into the initial process of particle formation which has not resulted in anything more than scanty evidence for a particular nucleation mechanism.

The molecular weight distribution, MWD, of an emulsion polymer reflects the types of events that contribute to polymer growth and particle nucleation processes. A theory for the MWD (developed by Lichti, et al. [1]) was compared with experimental data to obtain some insight into the particle formation mechanisms.

It was found that the experimental data could only be explained if coagulation between precursor particles occurred during the nucleation process. Subsequently it was proposed that particle nucleation was a two step mechanism, the first step being the formation of precursor particles by either the classical micellar entry or homogeneous nucleation processes and the second step the coagulation of the small precursor particles to form true latex particles.

- [1] Lichti, G., Gilbert, R.G. and Napper, D.H., Molecular Weight Distributions in Emulsion Polymerizations, *J. Polymer Sci. Polymer Chem. Edn.*, 18 (1980).

Photocorrosion of Colloidal Cadmium Sulfide, A Semiconductor

Rob Hayes (Melbourne)

Cadmium sulfide has been proposed as the basis of a photocatalyst for the production of H_2 from water by visible light. However, photocorrosion and subsequent breakdown of the cadmium sulfide support takes place upon irradiation.

The initial aim of the project is to gain some insight into the mechanism of, and the factors affecting, the photocorrosion. Attempts will then be made to prevent, or at least retard, this photocorrosive process.

The Growth of Poly(butylmethacrylate) Latex Particles

Lesli Halnan (Sydney)

The kinetics of emulsion polymerization of butylmethacrylate are being studied in order to obtain values for the rates of: entry into (ρ), exit from (k) and bimolecular termination (c) within the latex particles, as well as the importance of heterotermination of exited free radicals in the aqueous phase.

It is hoped that butylmethacrylate, a monomer which is insoluble in water, will represent an emulsion polymerization system in which the average number of free radicals per latex particle (\bar{n}) is high. If this is the case, the present studies will complete the following diagram:

	insoluble	"soluble" (monomer in water)
low \bar{n}	styrene $c \gg \rho, k$	vinyl acetate $k \gg \rho, c$
high \bar{n}	?	methyl methacrylate ρ, k dominate

The main experimental method for studying growth of the latex particles is dilatometry on seeded systems. The results of which should lead to values of ρ , k and c either by solution of the extended Smith-Ewart equations or by another theory which is yet to be developed.

Surface Phenomena in the Ultrafiltration of Colloids

R. McDonogh (NSW)

Using a membrane developed at the University of New South Wales, the interaction of SiO_2 sol ($r = 25 \text{ nm}$) and ultrafiltration (UF) membranes was studied. The membrane surface potential is pH dependent, with an isoelectric point at pH 5.5. Near the isoelectric point the membrane interacts with unstable colloid to produce a gel on the membrane surface. At pH 10 when the membrane is highly negative ($\zeta \sim -30 \text{ mV}$) the interaction with stable colloid gave no surface deposition. However, build up of colloid occurs below the membrane surface. The reason for this is thought to be due to effects on the colloid as it travels through the membrane matrix, including local concentration effects due to a tubular pinch.

A New Approach to Energy Site Distributions

Ian Metcalfe (Melbourne)

Using a Fast Fourier Convolution technique we propose a new method for extracting the energy site distribution, $F(E)$ from calorimetric data. By simultaneous evaluation of the adsorption isotherm and differential heats of adsorption data, we can not only calculate the shape of the distribution but also obtain an absolute energy scale.

It is to be hoped that using this general method, the difference in energy site distributions on a number of heat/silicon treated samples of titanium dioxide will be elucidated.

The method which uses a full B.E.T. adsorption isotherm will then be used to evaluate the energy site distribution on a wide range of gas/solid interface systems.

1983 Conference Song

Farewell and adieu to your health and to sanity
 Hello to Smith-Ewart, Hello to Lee White
 There's theory and experiment which lead to disparity
 So we worry all day, and we drink through the night.

So fill up your test tubes and fill up your beakers
 We've drunk all the beer and we've drunk all the wine
 We're making more sense now than when we were speakers
 We'll see you tomorrow; all up before 9.

My body is shaking, my voice it is quaking
 My eyes are all red and my brain isn't on
 I love playing cricket, I love picture-taking
 I love falling over and my name is Tom.

At the end of this conference our bosses will claim us
 We'll get in the bus or we'll get in our cars
 Then it's back to the labs - and one day we'll be famous
 But it won't be through science; we'll be video stars.

Chorus: We'll rant and we'll rave like true colloid chemists
 We'll rant and we'll rave like Tom, Bob and Don
 Until we return to the next student conference
 Its bloody hard going when experiments go wrong.

Last Chorus:

We'll rant and we'll roar like true colloid chemists
 We'll fart and we'll snore like the well-known Lee White
 And when we return to the next student conference
 The rest of the company will all sleep outside.

Warr Dunstan

(Sung to the tune "Augathella Station")