

**NINTH**  
**AUSTRALIAN COLLOID AND SURFACE CHEMISTRY**  
**STUDENT CONFERENCE**

**AUSTRALIAN NATIONAL UNIVERSITY**  
**(KIOLOA, N.S.W.)**

**1980**



**PROCEEDINGS AND ABSTRACTS**

COVER PHOTO

Scanning Electron Micrographs of monodisperse polystyrene latex particles after centrifugation. On the left is the disordered state found in the upper layers of sediment and on the right the hexagonal packing arrangement which develops in the lowest layers of the sediment when centrifugation induces coagulation.

from C. N. Bensley, "The Coagulation of Concentrated Colloidal Dispersions"

Ph. D. Thesis, The University of Sydney (1980).

PROCEEDINGS AND ABSTRACTS  
OF THE NINTH  
AUSTRALIAN COLLOID AND SURFACE CHEMISTRY  
STUDENT CONFERENCE  
KIOLOA, N.S.W., 1980  
AUSTRALIAN NATIONAL UNIVERSITY

CONTENTS

Preface and short history of the conference	1
Participants, 1980	5
Conference Programme	7
Abstracts	9

ACKNOWLEDGEMENTS

Contrary to the usual custom, we did not conduct an appeal to industry to raise funds for this, the Ninth Australian Colloid and Surface Chemistry Student Conference. Such an appeal would have conflicted with the extensive fund-raising required for the IUPAC-IUTAM International Symposium held in Canberra in March 1981. All participants in the Conference contributed financially but the bulk of the expenses was defrayed from the funds provided by the Universities of Melbourne and Sydney and the Australian National University. Accommodation and living expenses were kept to a minimum, with no sacrifice in quality by the superb organisation and splendid catering arrangements of our hosts from A.N.U. All participants thank our Canberra friends, especially the Conference Secretary, Steven Carnie, and the organisers and caterers Norma Chin, Derek Chan, Bernie Pailthorpe and Lee White for their tireless efforts to ensure a successful conference.

PREFACE

"Of the making of books there is no end, and in too much study there is much weariness of the spirit." So we are admonished by the Preacher in the Book of Ecclesiastes in his peroration (*Ecc.* 12; 12,13). It is a favourite quote and contains much wisdom. The views of the old goat on publications of conference proceedings are not recorded, but it seems unlikely that he would have been excessively enthusiastic. Couple this with, and contemplate the circumstance that this is the ninth Australian Colloid and Surface Chemistry Student Conference. Nine precedes ten, and a decade deserves celebration. But although as remarked by Ramanujan, the cube of 9 plus 1000 is the first number expressible as the sum of two cubes in two different ways [ $9^3 + 1000 = 1729 = 12^3 + 1^3 = 9^3 + 10^3$ ]; it is generally conceded that 9 is a singularly uninteresting number.

In other words the writer of this preface has an uphill job.

But there is some merit in recapitulating the history of the matter and in a reaffirmation of what this by how historic event is all about. The conference began in 1969, with R.J. Hunter, T.W. Healy and their students.

Despite a long and honourable tradition, and much good work, modern Australian Colloid and Surface Science was still in its infancy. The subject itself had not quite begun those astonishing revolutionary developments and expansion of its horizons which has taken it to centre stage of the physical, chemical and biological sciences, and indeed of engineering. There is probably no other discipline which underlies so much of technology - in paper, paint, pollution, photographic processes, soil science, minerals beneficiation, separation science, oil recovery, matters biomedical, detergents, cosmetics, water purification, food and beer, surface coatings - to name a few.

The Conference was designed to allow students and their supervisors from Australian Universities and Colleges to exchange research ideas, to give students an opportunity to present technical papers to a critical audience; to learn new experimental and theoretical skills; and to meet and learn from visiting industry and government scientists from this country and overseas. In this it has been eminently successful.

Australian research in the subject is now acknowledged to lead the world, and by some way. It is important that students going to industry and applied research be *au fait* with recent developments, and get to know the entire colloid and surface science community.

The last few years have seen a dramatic growth in activity in the subject and awareness on the part of industry of its increasing need for colloid and surface scientists. The formation of the RACI Division of Surface and Colloid Chemistry, its annual conferences, special meetings, new short courses to industry, grew out of the ASCSS Conference experience. IUTAM and IUPAC representing the senior international scientific unions in chemical engineering, fluid mechanics and pure and applied chemistry sponsored a major international meeting at Canberra, March 1981. The allied disciplines of electrochemistry and polymer science continue to expand.

Ultimately, however, despite this intense professional activity the (informal) Student Conferences remain, and will remain, as the benchmark and most important periodic cluster point for the community.

#### *Previous Meetings*

These conferences began in the late sixties as very informal gatherings (usually over a weekend) of the research students of Professors Healy (Melbourne) and Hunter (Sydney) respectively. Only student papers were permitted but in successive meetings the number of observers from other universities, the CSIRO, and Industry, gradually increased and the organisation became a little more formal.

The format usually consists of a one-day meeting with fairly wide attendance followed by a more secluded, residential arrangement for the weekend, during which the conference programme continues in an informal atmosphere with plenty of opportunity for small group discussion and social intercourse.

The 3rd Conference was in February 1972 in Sydney just before the 3rd Australian Electrochemistry Conference in Terrigal; most students also attended the latter meeting and some presented papers. The 4th meeting was in Melbourne, in May 1973, at the time of a one-day meeting of the Electrochemistry Division of the RACI, and was continued over the weekend at the University's field station at Blackwood near Ballarat,

Victoria. The 5th meeting was held at Sydney in November 1974 at the University and then over the weekend at the University's field station, Warrah House, Woy Woy, on the central coast. The 6th meeting was held at the Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, Canberra, in May 1976. The 7th meeting was held at the University of Melbourne in September 1977 and at Blackwood. The 8th meeting was held at the University of Sydney and at Yarrawood in November 1978.

These last six meetings have involved a significant number of observers (especially in the preliminary session) and have also involved participation by some additional, very active research groups, in particular the Applied Mathematicians from ANU, Dr. D.N. Napper's polymer colloids group (Sydney), some from Flinders University (Professor Bockris), and from the University of Western Australia (formerly Professor Quirk), as well as from the Royal Melbourne Institute of Technology and Swinburne College of Technology in Melbourne, the South Australian Institute of Technology in Adelaide, and from Professor Barnes' group at the University of Queensland.

Special Note

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

Associate Professor R.J. Hunter,  
Department of Physical Chemistry,  
University of Sydney,  
SYDNEY, N.S.W. 2006  
Australia

or

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

PARTICIPANTS - 1980

*From the University of Sydney, Department of Physical Chemistry*

Dr. R.J. Hunter, Associate Professor of Physical Chemistry  
Dr. D.N. Napper, Associate Professor of Physical Chemistry  
Matthew Ballard, Ph.D. candidate  
Colin Bensley, Ph.D candidate  
Bruce Chamberlain, B.Sc(Hons) candidate  
Dr. R. P. Chhabra, Post-Doctoral Fellow  
A. (Tony) Hodgson, Ph.D. candidate  
Gottfried Lichti, Ph.D. candidate  
Philip Limberg, B.Sc.(Hons) candidate  
Robyn Matarese, M.Sc. student  
Karen Scotman, B.Sc.(Hons) candidate  
D. Wood, B.Sc.(Hons) candidate

*From the University of Melbourne, Department of Physical Chemistry*

Dr. T.W. Healy, Professor of Physical Chemistry  
Dr. D.N. Furlong, Post-Doctoral Fellow  
Pam Freeman, Research Assistant  
J. Aston, B.Sc. (Hons.) candidate  
Eddie Blatt, Ph.D candidate  
Janice Grant, B.Sc. (Hons.) candidate  
Ian H. Harding, Ph.D candidate  
Louis O. Kolarik, Ph.D candidate  
Alice Lau, M.Sc. (Prelim.) candidate  
Robert Lamb, Ph.D candidate  
Brendan Lovelock, Ph.D candidate  
Ian M. Metcalfe, Ph.D candidate  
Russell Mills, B.Sc. (Hons.) candidate  
Daryl Williams, B.Sc. (Hons.) candidate

*From the South Australian Institute of Technology, School of Metallurgy*

Keith B. Quast, Ph.D candidate

*From the Broken Hill Proprietary Limited, Central Research Laboratory*

Dr. J.B. Smitham

*From the University of West Virginia, Department of Chemical Engineering*

Professor J.D. Henry Jr

*From the University of Bristol, School of Chemistry*

Dr. Brian Vincent

*From the Australian National University, Department of Applied Mathematics*

Dr. B.W. Ninham, Professor of Applied Mathematics

Dr. D.J. Mitchell, Senior Fellow

Dr. D.Y.C. Chan, Post-Doctoral Fellow

Dr. R.G. Horn, Post-Doctoral Fellow

Dr. B.A. Pailthorpe, Research Officer

Dr. L.R. White, Research Fellow

Lindsay R. Angel, Research Assistant

Steven L. Carnie, Ph.D candidate

Emma H.B. De Lacey, Ph.D candidate

Glen R. Walker, Ph.D candidate

Ian G. Watterson, Ph.D candidate

Norma Chin, Secretary

*From Tioxide Australia Pty Ltd, Tasmania*

Dr. David Rundle

*From Swinburne College of Technology, Chemistry Department*

Dr. Miles G. Hancock

*From C.S.I.R.O. Division of Mineral Chemistry, Port Melbourne*

Dr. G. Sparrow

NINTH AUSTRALIAN COLLOID AND SURFACE CHEMISTRY  
STUDENT CONFERENCE - 1980

PROGRAMME

Monday, 26th May

9.00 a.m.	"Stability of concentrated dispersions"	C. Bensley (Sydney)
9.25 a.m.	"Adsorption of heavy metals on an amphoteric latex"	I. Harding (Melbourne)
9.50 a.m.	"Rheological study of polymer flocculation"	R. Matarese (Sydney)
10.15 a.m.	"Surface tension minima of simple surfactant systems"	D. Williams (Melbourne)
10.40 a.m.	Morning Tea	
11.00 a.m.	"A study of the nylon/electrolyte interface"	B. Lovelock (Melbourne)
11.30 a.m.	"What is the Stern layer?"	S. Carnie (ANU)
12.00 noon	"Aerosol formation via homogeneous nucleation"	A. Hodgson (Sydney)
12.30 p.m.	Lunch	
2.00 p.m.	"Flotation of haematite using oleic and lauric acid"	K. Quast (SAIT)
2.30 p.m.	"Drag on a sphere in a viscoelastic fluid"	R. Chhabra (Sydney)
3.00 p.m.	"Temperature dependence of metal ion adsorption at the oxide/water interface"	A. Lau (Melbourne)
3.30 p.m.	Afternoon Tea	
3.45 p.m.	"Growth of polymer colloids"	G. Lichti (Sydney)
4.10 p.m.	"Adsorption on the magnetite surface"	L.O. Kolarik (Melbourne)
4.35 p.m.	"Stage III growth of polymer colloids"	D. Wood (Sydney)
6.30 p.m.	Conference Dinner	

[After dinner speaker: Professor J.D. Henry, University of West Virginia; Dr. Brian Vincent, Bristol University]

Tuesday, 27th May

9.00 a.m.	"Particles at interfaces"	R. Mills (Melbourne)
9.25 a.m.	"Rheology of colloidal dispersions"	P. Limberg (Sydney)
9.50 a.m.	"Controlled wettability of quartz surfaces"	R. Lamb (Melbourne)
10.15 a.m.	"Kinetics of methyl methacrylate emulsion polymerization"	M. Ballard (Sydney)
10.40 a.m.	Morning Tea	
11.00 a.m.	"Investigation of micelle interiors by fluorescence spectroscopy"	E. Blatt (Melbourne)
11.30 a.m.	"Dielectric spectroscopy of colloidal dispersions"	E. De Lacey (ANU)
12.00 noon	"Adsorption of non-ionic surfactants"	J. Aston (Melbourne)
12.30 p.m.	Lunch	
2.00 p.m.	"Anion adsorption on oxide surfaces"	J. Grant (Melbourne)
2.30 p.m.	"The primary electroviscous effect"	I. Watterson (ANU)
3.00 p.m.	"Heterocoagulation studies in magnetite/polystyrene systems"	I. Metcalfe (Melbourne)
3.30 p.m.	Coffee	
3.45 p.m.	"Flocculation of kaolinite suspensions by polymers"	K. Scotman (Sydney)
4.10 p.m.	"Polymerization of microemulsions"	B. Chamberlain (Sydney)

## ABSTRACTS

*The Coagulation of Concentrated Dispersions  
at Low Electrolyte Concentration*

Colin Bensley (Sydney)

The onset of rapid coagulation in dilute dispersion at high electrolyte concentrations ( $\approx 0.1 \text{ mol dm}^{-3}$  1:1 electrolyte) is a familiar phenomenon in colloid science. However, it is generally unappreciated that at high concentrations of colloid, rapid coagulation may occur at low electrolyte concentrations ( $< 10^{-2} \text{ mol dm}^{-3}$ ) even though the high particle surface potential would stabilise a dilute dispersion.

Dispersions of high colloid concentration and low electrolyte concentration exhibit measurable osmotic pressures which show a maximum as the volume fraction of colloid is increased. This maximum can be interpreted as the osmotic pressure at the maximum stable volume fraction and so measurements of this maximum, or coagulation, pressure can be used to judge theoretical models for particle interaction in concentrated dispersions. In the past this approach has been hampered by an invalid theoretical model of the coagulation process and some inexplicable experimental results. By examining coagulation as a diffusion process a valid theoretical approach is obtained, and new experiments have demonstrated a better correspondence between theory and experiment.

*Purification of Amphoteric Polystyrene Latices*

Ian H. Harding (Melbourne)

A series of amphoteric (zwitterionic) polystyrene latices were prepared having variable isoelectric point pHs (i.e.p.s) arising from acidic (methacrylic acid) and basic (dimethylaminoethyl methacrylate) functional groups of varying ratios. Each latex preparation was purified by various methods - ion exchange, dialysis, ultrafiltration and centrifugation/decantation; and characterised by various techniques - microelectrophoresis, surface tension, and conductometric and potentiometric titrations.

Although the purification methods of ion exchange and dialysis are well established, they have come under scrutiny in recent years and, in this study, were found to be unsuitable for the purification of high charge latex material having zwitterionic character. These methods, compared to the methods of ultrafiltration and centrifugation/decantation, showed high conductometric and potentiometric surface charges and low surface tensions for all latex samples, indicating the presence of impurities. In contrast, however, all purification methods gave the same isoelectric point for a given latex sample.

*The Flow Behaviour of Polymer Flocculated Colloidal Latex Suspensions*  
Robyn Matarese (Sydney)

The elastic floc model provides an excellent basis for the description of the flow behaviour of salt-coagulated colloidal dispersions. Such systems exhibit plastic-pseudoplastic behaviour with a well defined Bingham Yield Value,  $\tau_B$ , and a critical shear rate,  $D_0$ , above which the shear stress versus shear rate plot becomes linear. The slope of this linear portion defines the plastic viscosity  $\eta_{PL}$ .

According to the elastic floc model the flow units at high shear rate are more or less open flocs containing some hundreds of particles. The value of  $\eta_{PL}$  is determined by the degree of openness of the floc (i.e. the amount of trapped solvent). The  $D_0$  value measures the force required to separate two flocs whilst the  $\tau_B$  value measures the total energy dissipated during the collisional interaction between two flocs.

In the present work an attempt will be made to apply these ideas to the analysis of the flow behaviour of a suspension which has been flocculated by a long-chain polymer. The particles are highly monodisperse, negatively charged poly-methylmethacrylate spheres and the flocculating polymer is a cationic polymer supplied by Catoleum P/L (their Alfloc 8101). Experiments were conducted at pH 4 (when the polymer is highly positively charged) at pH 7 and at pH 10 (when it is uncharged).

*Surface Tension Minima of Polymer Flocculation*  
Daryl Williams (Melbourne)

The surface tension behaviour of aqueous solutions of oleic acid has been investigated as a function of pH. A maximum in the surface tension was observed at high pH and a minimum at neutral pH.

The minimum in surface tension may be explained by the model proposed by Beunen *et al.* (1). Current understanding of the solution chemistry of oleic acid does not explain the surface tension maximum.

(1) J.A. Beunen, D.J. Mitchell and L.R. White, *Trans. Faraday Soc.* I 74, 2501 (1978).

*Calculation of Inner Layer Capacitances*  
*from Charge and Potential Data*  
Brendan Lovelock (Melbourne)

The electrical double layer at the interface between non-conducting solids and aqueous electrolyte solutions has in the past, been relatively poorly described in terms of classical Gouy-Chapman-Stern-Graham (GCSG) theory. Most current descriptions rely on surface site-ion binding to model the e.d.l. on materials such as inorganic oxides, latex colloids, clay minerals, etc. It must be stressed that these site models invariably involve, more or less, usage of GCSG theory.

In efforts to provide more experimental input, Smith *et al.* (1,2) have used three experimental quantities to help minimise the number of adjustable parameters. Thus they use, in addition to the surface charge ( $\sigma_0$ ) and zeta potential ( $\zeta$ ) data as a function of say pH and salt concentration, the quantity  $(d\zeta/dpH)_{\zeta=0}$  also as a function of salt concentration. This allows elimination of one more adjustable parameter. Our current study has shown that considerably more progress of this kind can be made if a fourth quantity  $(d\sigma_0/dpH)_{\sigma_0=0}$  is also used and classical GCSG theory is invoked.

If the surface, Stern and diffuse layer planes have charges of  $\sigma_0$ ,  $\sigma_\beta$  and  $\sigma_d$  respectively and potentials of  $\psi_0$ ,  $\psi_\beta$  and  $\psi_d = \zeta$  respectively, and if the inner and outer capacitances of the inner region are  $K_1$  and  $K_2$ , then at  $\zeta = \sigma_0 = 0$ , i.e. no specific adsorption at the p.z.c./i.e.p.

$$K_1^{-1}(d\sigma_0/dpH) = K_2^{-1}(d\sigma_d/dpH)_{\zeta=0} + (d\psi_0/dpH)_{\zeta=0} - (d\psi_d/dpH)_{\zeta=0}.$$

The first term on the right hand side is obtained from experimental data

and the G.C. equation while the third term on the right hand side and the coefficient of  $K_1^{-1}$  on the left hand side are likewise experimentally determined. If the terms in  $K_1$  and  $K_2$  and the term in  $\psi_0$  are assumed to be independent of salt concentration, then if  $(d\sigma_0/dpH)_{\sigma_0=0}$  at say three salt concentrations is plotted as a function of  $(d\zeta/dpH)_{\zeta=0}$ ,  $K_1$ ,  $K_2$  and  $(d\psi_0/dpH)_{\zeta=0}$  can be determined uniquely.

- (1) A.L. Smith, *Dispersions of Powders in Liquids* (G.D. Parfitt, ed.), Chap. 3. Applied Science Publishers Ltd., London, 2nd ed., 1973.
- (2) A.L. Smith, *J. Colloid Interface Sci.* 55, 3 (1976).

#### *What is the Stern layer?*

Steven L. Carnie (ANU)

Results from a recent attempt to model the properties of the Stern region in the electrical double layer will be described. The model treats both the ions and solvent molecules in an electrolyte as distinct molecular species - the solvent is *not* assumed to be a dielectric continuum. The properties of the Stern layer - which results from solvent structure at the charge surface, are not postulated *a priori* but emerge naturally from the model. The nature of the Stern layer depends on the properties of the solvent as well as that of the charged surface.

#### *Aerosol Formation in Expanding Gas Flows*

Tony Hodgson (Sydney)

The formation of aerosols from the gas phase is of great theoretical and practical importance. In order to understand complicated processes such as air pollution and cloud formation, homogeneous nucleation (the simplest mechanism for aerosol formation) needs to be understood.

A great deal of controversy surrounds homogeneous nucleation theory, especially concerning the replacement factor (involves translational and rotational motions). Also, the application of bulk properties (such as surface tension) to tiny microclusters containing as few as five molecules is very doubtful. In order to avoid these theoretical problems, a number of workers have calculated cluster properties from inter-molecular potentials and assumed cluster structures.

The double diaphragm shock tube technique, where the test gas is first heated and then rapidly cooled, has been used to study the homogeneous nucleation of cyclohexane. A computer analysis of the gas

flow, coupled to light scattering measurements, gives conditions under which nucleation occurs. A nucleation rate can be fitted to this data and comparison made with the various theories.

In future experiments it is hoped to study zinc by evaporating a zinc aerosol to produce zinc vapour which subsequently cools and nucleates. Comparison of cluster calculations with such experiments would be easier than with earlier experiments, where complicated systems such as water and ethanol have been studied.

#### *Flotation of Hematite Using Oleic and Lauric Acids*

Keith B. Quast (S.A.I.T.)

The flotation behaviour of oxide minerals using fatty acids was examined using saturated and unsaturated fatty acids to float iron oxide in the form of hematite. Oleic acid has been extensively tested as a collector for hematite, but little is known about the flotation behaviour of lauric acid. Both reagents are said to chemisorb onto the hematite surface prior to flotation. From solution equilibria it is known that lauric acid is more soluble in water than oleic acid; however, its shorter chain length could reduce its collecting power, and thus the reagents should show similar flotation behaviour.

The hematite sample used in the test work had an iep of 2.7 and a zpc of 6.7, the difference being due to the fine silica present in the natural sample of hematite. The test work showed the effect of pulp density during conditioning, conditioning times, and the way the collector is added on the flotation of hematite. The flotation recovery using both collectors is also highly dependent on the pH, with low recoveries below pH 2, and only moderate recoveries between pH 8.5-9.0 compared to other values of pH. No explanation for the recovery "trough" at pH 8.5-9.0 could be offered, although this same phenomenon has been reported for a number of different minerals with lauric acid.

#### *The Temperature Dependence of the Adsorption of Hydrolysable Metal Ions at Oxide/Water Interface*

Alice Lau (Melbourne)

The adsorption of hydrolysable metal ions at oxide/water interface has been widely studied by many researchers in the past. However, our interest is to investigate the effect of temperature on the adsorption

parameters such as the hydrolysis of metal ions; the precipitation of metal ions as hydroxides; the solubility and electrokinetic properties of oxides, etc. And finally, its effect on the adsorption mechanisms.

Titanium dioxide and cadmium ions are chosen as the model oxide and metal ions respectively. And the experiments are done in  $10^{-3}$  M  $\text{KNO}_3$  electrolyte solution at temperatures of 10 °C, 25 °C and 50 °C.

*The Growth of Polymer Colloids: Latex Particle Disaggregation Processes*  
Gottfried Lichti (Sydney)

It is widely believed that latex particles, once formed in a styrene emulsion polymerisation, consist of homogeneous concentrated solutions of polymer in monomer. The particles are thought to be stable independent entities during the majority of the polymerisation reaction. These notions are challenged by the results of an investigation of styrene emulsion polymerisation using two new techniques, which strongly suggest that in certain cases, latex particles are composite entities, consisting of aggregates of smaller latex particles. These composites may disaggregate during the course of the reaction. The new techniques are: (i) the direct measurement of the evolution in time of the particle size distribution of the growing latex, and (ii) the freeze-fracture method which eliminates many of the artifacts of conventional transmission electron microscopy.

*Adsorption on the Magnetite Surface*  
Louis O. Kolarik (Melbourne)

Small particles (1-10  $\mu\text{m}$ ) of magnetite are used in a new water purification process called Sirofloc. In the process, negatively charged impurities such as humic acids, clays and biocolloids from water are adsorbed on the positively charged magnetite particles. Magnetite can be used alone or in conjunction with another coagulant or flocculant. The used magnetite particles can be reactivated with alkali and reused repeatedly.

Interaction of natural  $\text{Fe}_3\text{O}_4$  with  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ , a synthetic cationic polyelectrolyte and bentonite clay was studied. A novel magnetic streaming potential technique was developed and used. In this

technique, a plug of magnetite is formed and held in the cell by magnetic forces rather than by mesh or perforated electrodes.

It was found that the electrokinetic properties ( $\zeta$  potential and iep) of magnetite are controlled by Al or Fe hydrolysis species deposited on the surface. The extent of the changes depended on the concentration of the species. Similarly, a long chain cationic polyelectrolyte (Cyanamid C573, m.w.  $\sim 10^4$ ) and  $\text{Ca}^{2+}$  ions can be adsorbed. In all cases the deposition commenced in the vicinity of the magnetite iep. While addition of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  caused a shift in iep only, charge reversal was observed in the case of P.E. and  $\text{Ca}^{2+}$ . The magnetite- $\text{Ca}^{2+}$  interaction mechanism is not clear.

Heterocoagulation in the magnetite-bentonite system alone and in conjunction with cationic P.E. (C573) was also studied using light scattering. It was shown that the capacity of magnetite to adsorb clay is, at fixed particle size of  $\text{Fe}_3\text{O}_4$  and clay, a function of the concentration of the particles, pH and ionic strength of the aqueous medium. In the presence of P.E. it is also a function of P.E. concentration.

*Particle Size Distributions in Interval III  
of an Emulsion Polymerisation*  
D. Wood (Sydney)

The theoretical prediction of particle size distributions in interval III of an emulsion polymerisation reaction depends essentially upon a knowledge of the particle growth rate and the way in which it varies as the reaction proceeds. The problems which arise in the treatment of interval III are closely linked with the disappearance of free monomer droplets and the consequent behaviour as the monomer within the latex particles is depleted.

At present, interval III can be handled theoretically up to perhaps 90% conversion; the limitation here is that the rapid exchange of monomer between the particles via the aqueous phase is no longer viable due to viscosity effects within each particle. However, while the rapid exchange mechanism does operate, the particle growth rate assumes a simple time dependence which facilitates the treatment (actually, the situation is complicated slightly after about 50% conversion due to the onset of the viscosity effects). Beyond this region, the problem becomes

almost intractable as the growth rate becomes a many-variable function, although in certain special cases some approximate methods may find application.

#### *Particles at Interfaces*

R. Mills (Melbourne)

The stability of a particle at an interface was investigated both theoretically and experimentally. Two approaches were used for the theoretical study of stability. They were: (1) a free energy analysis, (2) a force balance analysis. The force balance approach formed the basis for a computer programme which was used to determine the effect of various parameters and particularly the interfacial curvature ("wall-effects") on particle stability. This was combined with an experimental programme and there was found to be a general agreement between theory and experiment.

#### *Commissioning of a New Couette Rotational Viscometer*

Philip Limberg (Sydney)

A commercial rotoviscometer was purchased (Haake RV2) and it was found to be unsuitable for measuring viscosities of less than 2 cp. It was necessary to modify the rotoviscometer and establish its operation for measuring viscosities of this magnitude.

It was first necessary to establish a procedure for measuring the viscous behaviour of water and water/glycerol mixtures and correlate the observed shear stress-shear rate behaviour with that for the same material in an Ostwald (capillary) viscometer.

The shear stress-shear rate behaviour for such systems (water/glycerol) was compared with that obtained in an older Couette apparatus.

Finally the shear stress-shear rate behaviour of a coagulated sol, in the modified Haake RV2, was compared with that in the older Couette to see how they correlated.

#### *Controlled Wettability of Quartz Surfaces*

Robert Lamb (Melbourne)

The wettability of flat quartz crystal surfaces has been assessed by measurement, at 25 °C of contact angle at the water vapour/water drop/

quartz plate three phase line. Plates pretreated by heating in vacuum gave angles, measured through the drop one minute after removal from vacuum, of zero to 44° as pretreatment temperature was increased from 200 to 1000 °C. Fully hydroxylated, therefore hydrophilic, quartz surfaces are progressively rendered hydrophobic by mutual condensation of surface hydroxyls to form siloxane bridges. Hysteresis was at a maximum after heating at 700 - 800 °C indicating that maximum surface chemical heterogeneity was produced by heating in this temperature range. Plates methylated subsequent to heat treatment gave angles that were constant at around 80° up to treatment at 600 °C and that decreased from 80 to around 47° as pretreatment temperature was further increased to 1000 °C. This variation with temperature is consistent with a mechanism for methylation in which only non-hydrogen bonded surface hydroxyl groups on quartz are reactive towards methylating reagent. Contact angles on both heat-treated and methylated plates were observed to decrease following extended exposure to water vapour.

*The Kinetics of the Emulsion Polymerisation  
of Methyl Methacrylate*  
Matthew Ballard (Sydney)

The behaviour of methyl methacrylate in seeded systems has been studied for the first time. In the initiator concentration range  $0 - 3 \times 10^{-2} \text{ mol dm}^{-3}$ , the steady-state rate of reaction was found to vary by a factor of approximately 100. No plateau region was observed in the variation of rate of reaction with initiator concentration, contrary to most predictions. Observation of the approach to steady-state enabled the value of the exit rate constant  $k$  to be determined as  $(8.3 \pm 2.7) \times 10^{-3} \text{ s}^{-1}$ , and the variation of the entry rate constant  $\rho$  was found to be

$$\rho = \rho_0 + 0.29 [I]^{0.71} \text{ s}^{-1},$$

where  $\rho_0$  was the measured thermal entry rate constant,  $\rho_0 = (6.8 \pm 1.5) \times 10^{-5} \text{ s}^{-1}$ , and  $[I]$  was the initiator concentration. Further work is under way to refine the values for these rate constants and to investigate the "Trommsdorff Gel" effect, a region of very high rates of reaction.

*Investigation of Micelle Structure  
by Fluorescence Spectroscopy*  
Eddie Blatt (Melbourne)

Micelles are molecular aggregates formed in solutions of detergents. Their structure has been investigated for a number of years and using a variety of experimental and mathematical techniques. Fluorescence spectroscopy techniques using small aromatic molecules as probes, however, have only recently found application. The position of the probe in the micelle is of crucial importance.

Using a series of *n*-(9-anthroyloxy) fatty acids ( $n = 2, 6, 9, 12$ ) sensitive to polarity and fluidity gradients of lipid bilayers, the structure of the micelle sodium dodecyl sulphate has been investigated. Fluorescence quenching experiments and spectral characteristics of emission from the probes indicate an increasing polarity gradient from the core to the surface of the micelle.

*Electrophoresis and the Sedimentation Potential*  
Emma de Lacey (ANU)

The fundamental equations of electrophoresis are set up. These describe what happens when an electric field is applied to a colloidal particle in an electrolyte. The sedimentation potential is discussed as an example. It provides a method of measuring zeta potentials experimentally without having to follow the movement of the particle, unlike with most other techniques.

*Adsorption of Non-Ionic Surfactants*  
J. Aston (Melbourne)

The adsorption of a series of polyoxyethylene nonylphenol ethers, with distributions of components of differing ethylene oxide chain lengths was studied for hydrophilic and hydrophobic silica surfaces. The hydrophobic silica was prepared synthetically by replacement of surface hydroxyls with Trimethyl Silane (TMS) groups. The surfactant distributions were described by the Poisson equation and had mean molar ratios for ethylene oxide/nonylphenol of 9, 13, 20, 40, 100 such that a range of hydrophile (EtO chain)/hydrophobe (nonylphenol) ratios were studied.

The bifunctional character of the polyoxyethylene nonylphenols was studied by determining the adsorption isotherms of the surfactant mixtures

with differing EtO chain lengths, as a function of the hydrophobicity of the surface. It was found that there was a dependence on the chain length for both the hydrophilic and hydrophobic surfaces. However, this dependence was greater for the hydrophilic case.

Using the isotherms and the Langmuir model of adsorption the free energies of adsorption were determined for each of the surfactant mixtures. The role of the EtO chain during adsorption was considered and it was concluded that the adsorption probably results from competition between the solid substrate and the surfactant micelle.

*Anion Adsorption on Oxide Surfaces*  
Janice Grant (Melbourne)

Adsorption of aqueous silica on titanium dioxide, alumina, goethite and latex has been studied as a function of pH.  $\text{TiO}_2$  exhibited a clear maximum in adsorption at a pH equal to the pKa of monosilicic acid. This adsorption behaviour was adequately described by a simple free energy model. Goethite did not display a maximum in adsorption at a pH equal to the pKa of the acid. A surface complexation model was capable of explaining the goethite data. Adsorption of silica on alumina showed no clear pKa dependence and adsorption densities in excess of a monolayer coverage were observed. The precipitation, either in bulk or at the surface, of aluminosilicates was invoked to explain this enhanced adsorption. Amphoteric latex did not show a pH dependence and was shown to have a much lower affinity for the silicate ions than the other colloids in this study. The results indicate that the chemistry of the substrate is of vital importance in the removal of aqueous silica from solution.

*The Primary Electroviscous Effect in Suspensions of Charged Spherical Particles*  
Ian G. Watterson (ANU)

The effective viscosity  $\eta$  of a suspension of charged spherical colloidal particles in a general electrolyte of viscosity  $\eta_0$  is calculated to first order in the volume fraction  $\phi$  to be

$$\eta = \eta_0 \left[ 1 + \frac{5}{2} \phi [1 + p(\zeta, \kappa a)] \right].$$

The primary electroviscous coefficient  $p(\zeta, \kappa a)$  as a function of the zeta

potential  $\zeta$  is derived in terms of the asymptotic behaviour of the hydrodynamic flow field far from a typical colloidal particle. The computation of  $p(\zeta, \kappa a)$  (for a general mixed electrolyte with  $\zeta$  unrestricted in magnitude) is reduced to the solution of a set of linear coupled ordinary differential equations and an accurate and robust numerical scheme for solving them demonstrated. An analytic approximate expression for  $p(\zeta)$  correct to  $O(\zeta^2)$  is derived and shown to agree with an early result of Booth (1). Exact numerical results are compared with the approximate expression of Booth.

A maximum is predicted in the primary electroviscous coefficient  $p(\zeta)$  for all  $\kappa a$  values. The measurement of this maximum may be used to test the validity of the underlying equations.

(1) F. Booth, *Proc. Roy. Soc.* 203, 533 (1950).

*Electrokinetics (Zeta) Potentials of Magnetic Ion Oxides*  
I. Metcalfe (Melbourne)

The streaming potential technique has been used to determine the zeta potential behaviour of magnetic iron oxides ( $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{CoFe}_2\text{O}_4$ ) as a function of pH and salt concentration. These colloidal iron oxides are held in the form of a plug by means of external magnets. The streaming potential  $\Delta E$  is measured as a function of fluid flow induced by a pressure drop  $P$ . The magnetically held plug is found to obey the requirements of the streaming potential technique and an isoelectric pH (i.e.p.), independent of added salt concentration, is observed. However, if one uses the conductance of electrolyte in the plug in the standard formula, the calculated zeta potentials are very much lower than other oxides. At a given pH, the zeta potentials show an increase in magnitude (rather than the conventional decrease) with increasing salt concentration.

Low zeta potentials are classically attributed to a second conductance pathway back through the plug for the conduction current ( $I^{\text{cd}}$ ). Generally, this is due to double layer conductance (surface conductance); however, for the loosely packed magnetic plugs, which are 90% (by volume) solution, these studies indicate surface conductance is unimportant. Magnetite single crystals, however, conduct ( $\lambda_{\text{crystal}} = 200 \Omega^{-1} \text{cm}^{-1}$ ) such that if the plug is considered to be a pair of resistors in parallel, viz.  $R_e$ , for electrolyte in the plug, and  $R_x$  for the magnetite itself, it is found that the zeta potential-pH-salt behaviour is similar to that of

other oxides. The conductivity assigned to a conduction path through the magnetite of the plug is some very small fraction of bulk magnetite conductivity, indicating that contact between the magnetic particles is not perfect and/or that electrolyte-magnetite electron transfer is limited in some way. Confirmation of the concept of conduction through the particles of the plug was provided when silica coated magnetite gave normal zeta potential behaviour.

*Flocculation of Kaolinite by Anionic Polymers*  
Karen Scotman (Sydney)

Kaolinite forms flat hexagonal shaped platelets. The faces of the platelets are negatively charged while the charge on the edges is pH dependent. At low pH they are positively charged and as the pH is raised the number of positive charges decreases. Because of the nature of the charged surface, different types of interactions occur between particles, depending on the pH. At low pH there exists a strong electrostatic interaction between the positive edges and the negative faces forming a card-house type of structure. At neutral pH, the card house structure opens out and becomes more extended forming long strings of particles. At high pH, the particles are separate because of the repulsion between the negative surfaces.

Addition of an anionic polymer at various pH's will affect the particle interactions. The various interactions are correlated from an interpretation of the rheological behaviour, sedimentation volume and zeta potential of the solution. Results of flocculated kaolinite at pH 7 can be interpreted as disruption of edge-face interactions on addition of polymer. At pH 4.5 a small addition of polymer shows the same effect as increasing the pH (i.e. opening the floc structure) and further additions of polymer disrupt the particle interactions.

*Polymerisation of Microemulsions*  
Bruce Chamberlain (Sydney)

The characteristics and methods of preparation of microemulsions are outlined. A method for the preparation of a microemulsion of styrene in water is given. It was noted that the locus of polymerisation in microemulsions is uncertain, hence a study of "true" emulsion polymerisation was undertaken. In "true" emulsion polymerisation free radical species enter directly into the emulsion droplets causing polymerisation to occur

within the droplets, compared to aqueous phase initiation followed by polymerisation within polymer particles in normal emulsion polymerisation.

A preliminary kinetic study of the "true" emulsion polymerisation of a styrene in water system, stabilised by a sodium dodecyl sulphate/dodecanol surfactant mixture is outlined. Four regions are distinguished on a generalised per cent conversion versus time curve. The first, a region of increasing rate, due to an increase in  $\bar{n}$ , the second, a pseudo-steady state region, the third a decreasing rate region, due to first order decay of monomer, and the fourth a region where the Trömsdorff effect manifests itself.