

FIFTH
AUSTRALIAN
COLLOID AND SURFACE CHEMISTRY
STUDENT CONFERENCE

UNIVERSITY OF SYDNEY

1974



Proceedings and Abstracts

COVER PHOTOGRAPHS

- TOP LEFT - Electron micrograph of hydrated aluminium oxide (Bayerite) particles prepared by ageing alkaline Al(III) aqueous solutions; magnification 1×10^5 .
(Elizabeth Bate, University of Melbourne)
- TOP RIGHT - Pre-shadowed carbon replica of a freeze-dried Ca-illite assemblage. Regular packing of individual Ca-illite crystals is clearly visible on the surface of the assemblage; magnification 32,000X.
(Richard Greene, University of W.A.)
- LOWER CENTRE - Optical micrograph of a large 20μ PbS (galena) particle of zeta potential -25 mV with adherent colloidal iron oxide (goethite) flocs of zeta potential +10 mV; magnification 4000.
(Bruce Firth and Paul Neville, University of Sydney)

PROCEEDINGS AND ABSTRACTS
OF THE FIFTH
AUSTRALIAN COLLOID AND SURFACE CHEMISTRY
STUDENT CONFERENCE
SYDNEY, 1974

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Acknowledgements

Student and Staff participants contributed in part to the running of the Conference. However, the major financial support came from generous donations by the Universities of Sydney and Melbourne, A.N.U., Peko-Wallsend, B.H.P., Monsanto (Australia), Albright and Wilson (Australia), C.S.R. Research, Hardman Research, N. B. Love, M. D. Research and Union Carbide.

All concerned with the meeting thank these sponsors for making this and other Australian Colloid and Surface Chemistry Student Conferences possible.

PREFACE

Colloid and Surface Science is concerned with processes and systems in which the surface of the material exerts a controlling influence on the properties of the system. *Aerosols* - small droplets of liquid dispersed in air, *clays* - small solid particles dispersed in liquids, *emulsions* - small droplets of one liquid dispersed in another, *blood* - small biocolloid platelets dispersed in a fluid, *photographic film* - small silver halide particles dispersed in a gel matrix; these examples illustrate the wide range of material, biological and technological processes of concern to the colloid chemist.

Because of the diversity of disciplines involved in colloid and surface science, education and research training in the subject exposes the student to theoretical and experimental skills not only in chemistry but also in physics, biology and engineering. In order to foster these interdisciplinary aspects of colloid science, the Australian Colloid and Surface Chemistry Student Conference was begun in 1969 and the present volume outlines the programme and contents of the fifth such conference.

The conference is 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 on their research work to a critical audience, to learn new experimental and theoretical skills and to meet with and learn from visiting industrial and government scientists.

The fifth student conference was held at the School of Chemistry, University of Sydney and at Warrah House, Woy Woy, from November 7 - November 10, 1974 by students from the Universities of Sydney, Melbourne, West Australia, The Flinders University of South Australia and the Australian National University, Canberra. Two invited papers by Dr H. J. L. Wright of Imperial College, London and Dr A. Homola, University of Melbourne, were included in the programme. Also participating in the discussion were a number of University, industry and government research scientists.

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,
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or

Dr T. W. Healy,
Reader in Physical Chemistry,
University of Melbourne,
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*PARTICIPANTS - 1974*From the University of Sydney, Department of Physical Chemistry -

Dr R. J. Hunter, Associate Professor of Physical Chemistry
Dr D. H. Napper, Senior Lecturer in Physical Chemistry
Robert Evans, Ph.D. Candidate
Bruce Firth, Ph.D. Candidate
Brian Hawkett, B.Sc.(Hons.) Candidate
Jean V. Leyendekkers, Research Fellow
Paul Neville, M.Sc. Candidate
Jim Smitham, Ph.D. Candidate

From the University of Melbourne, Department of Physical Chemistry -

Dr T. W. Healy, Senior Lecturer in Physical Chemistry
Dr R. O. James, A.R.G.C. Postdoctoral Fellow
Dr A. Homola, A.P.M. Postdoctoral Fellow
Elizabeth Bate, B.Sc.(Hons.) Candidate
Margaret Donnan, M.Sc. Candidate
Alan Durbridge, B.Sc.(Hons.) Candidate
Robert Jung, M.Sc. Candidate
Michael Moignard, M.Sc. Candidate
John Ralston, Ph.D. Candidate and Lecturer in Chemistry,
Swinburne Institute of Technology, Melbourne
Pauline Stiglich, M.Sc. Candidate
David Yates, Ph.D. Candidate

From the Australian National University, School of Applied Mathematics -

Dr John Perram, Research Fellow
Derek Chan, Ph.D. Candidate
Lee White, Ph.D. Candidate
Chris Barnes, Ph.D. Candidate
Cliff White, Ph.D. Candidate
Jacek Duniec, Ph.D. Candidate

From The Flinders University of South Australia, School of Physical
Sciences -

M. A. Habib, Ph.D. Candidate

From The University of West Australia, Department of Soil Science -

Michael Boland, Ph.D. Candidate

Richard Green, Ph.D. Candidate

Brian Kavanagh, Ph.D. Candidate

From The West Australian Institute of Technology -

Dr A. Parentich, Senior Lecturer in Chemistry

From Imperial College, London -

Dr Harley J. L. Wright (now at C.S.R. Research)

From CSIRO Division of Mineral Chemistry -

Dr Len Warren

From Industrial Research Groups -

Lynne C. Barnett, Albright and Wilson (Australia)
(former M.Sc. Candidate at Sydney)

Dr Stuart Nicol, B.H.P.

Dr Alan Dun, Research Director, Monsanto

Dr John Friend, Davis Gelatine

Dr David Lloyd, Chief Research Chemist, N. B. Love

Mark Wilson, C.S.R. Research

Kevin Monfort, Union Carbide

AUSTRALIAN COLLOID AND SURFACE CHEMISTRY

STUDENT CONFERENCE 1974

PROGRAMME

Thursday, November 7th - School of Chemistry, University of Sydney

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|-----------|---|----------------------|
| 5.00 p.m. | "Rheology of Suspensions" | B. A. Firth (Sydney) |
| 5.45 p.m. | "Charge Regulation at
Amphoteric Surfaces" | Derek Chan (A.N.U.) |

Friday, November 8th - School of Chemistry, University of Sydney

- | | | |
|------------|--|------------------------------------|
| 10.00 a.m. | "Dewatering of Slurries" | Dr Harley J. L. Wright
(London) |
| 10.30 a.m. | "Titration and Exchange
Studies on Oxides" | David Yates
(Melbourne) |
| | 11.00 a.m. Morning tea/coffee | |
| 11.30 a.m. | "Adsorbed Polymer Layers
on Oxides" | Brian Kavanagh (W.A.) |
| 12.00 noon | "Analytic Theories of
Steric Stabilisation" | Jim Smitham (Sydney) |
| 12.30 p.m. | "Kinetics of Emulsion
Polymerisation" | Brian Hawkett
(Sydney) |
| | 1.00 p.m. Lunch | |
| 2.30 p.m. | "Adsorption of Polymers
at Interfaces" | Lee White (A.N.U.) |
| 3.00 p.m. | "Adsorption of Oleic Acid
on Iron Oxide" | Robert Jung
(Melbourne) |
| | 3.30 p.m. Afternoon tea/coffee | |
| 4.00 p.m. | "Coagulation of Polymer
Latices" | Dr Andrew Homola
(Melbourne) |
| | Evening Conference Dinner (at Ettalong) | |

Saturday, November 9th - Warra House, Woy Woy

- | | | |
|-----------|---|--------------------------------|
| 9.00 a.m. | "Coagulation of Colloidal
Cellulose" | Margaret Donnan
(Melbourne) |
|-----------|---|--------------------------------|

6.

9.40 a.m.	"Water Molecule Orientation in the Electrical Double Layer"	M. A. Habib (S.A.)
10.15 a.m.	"Adsorption of Quaternary Ammonium Ions at the DME"	Lynne C. Barnett (Sydney)
11.00 a.m.	Morning tea/coffee	
11.30 a.m.	"Zeta Potential of Zinc Sulphide"	Michael Moignard (Melbourne)
12.15 p.m.	"Slime Coating of Sulphides"	Paul C. Neville (Sydney)
1.00 p.m.	Lunch	
2.30 p.m.	"Adsorption of Cd(II) on Oxides"	Pauline Stiglich (Melbourne)
3.10 p.m.	"Charge Behaviour of Kaolinite"	Michael Boland (W.A.)
3.50 p.m.	Afternoon tea/coffee	
4.15 p.m.	"General Discussion"	
	Evening Barbecue, Woy Woy	

Sunday, November 10th

Warra House, Woy Woy

9.15 a.m.	"Electron Microscopic Tech- niques in the Study of Colloidal Dispersions"	Richard Green (W.A.)
10.00 a.m.	"Precipitation of Colloidal Dispersions"	Elizabeth Bate (Melbourne)
10.30 a.m.	"Photochemical Surface Reactions"	Alan Durbridge (Melbourne)
11.00 a.m.	Morning tea/coffee	
11.30 a.m.	"Surface Properties of Asbestos Minerals"	John Ralston (Melbourne)

ABSTRACTS

"Rheology of Suspensions"

Bruce Firth (Sydney)

Certain sterically stabilised latices can be rendered unstable by raising the temperature. The rheological behaviour of such unstable systems was investigated by considering aggregation of the particles by Brownian and shear collisions and rupture of the aggregates by shear field forces. A set of rate equations were derived for the above physical processes and these were solved numerically to find the number distributions of various sized aggregates at a number of shear rates.

Plastic and elastic creep stress models were derived and compared with experimental creep stress data. The elastic model described the general features of the flow curve but it also indicated that an additional energy dissipating process was occurring in a flowing suspension. It is suggested that this process is the movement of solvent between aggregate particles as the aggregate is stretched and compressed by the shear field. A model is being developed to test this assumption.

"Charge Regulation at Amphoteric Surfaces"

Derek Chan (A.N.U.)

This paper is a theoretical study of the double layer interaction between identical planar amphoteric surfaces. Each surface is considered to develop a surface charge by the association and dissociation of ionizable surface groups. The interaction is assumed to be at electrochemical equilibrium. An adsorption isotherm for potential determining ions can then be derived relating the surface charge and the surface potential in a self-consistent manner. This is used in place of the usual constant charge or constant potential boundary condition. Numerical calculations based on model systems for hydrous oxides are given. The relation between this new boundary condition and the constant charge or potential approximation is discussed.

"The Dewatering of Clay Suspensions"

H. J. Wright

(in association with J. A. Kitchener, Imperial College)

The problem of dewatering highly stable smectite slurries was considered from a colloid chemical point of view. The need for appropriate salts to destabilise these suspensions was noted.

The filtration of compressible filter cakes was then discussed. It was shown that the filtration rate is dependent upon two parameters; the *permeability* and the *solids pressure*. These parameters could be obtained experimentally for different solids concentrations as a cake was dewatered in a particular manner. Experimental values were obtained for clay cakes formed from coagulated and flocculated suspensions of montmorillonite and Laponite (a synthetic clay made by Laporte). The effects of different concentrations of magnesium sulphate and polyethyleneoxide on the cake properties were investigated.

The differential equations governing the filtration of compressible cakes were solved for selected combinations of solids pressure and permeability behaviour. Theoretical flow curves for filtration under constant pressure were thus obtained. It was noted that by using appropriate cake parameters one could hypothetically formulate two cakes which deviated at different rates and which had intercepting dewatering curves. Such conditions might be achieved by the prior colloid chemical treatment, and the result is of significance in deciding how to treat a slurry which is to be filtered to a predetermined moisture content as quickly as possible.

"Titration and Exchange Studies on Oxides" David Yates (Melbourne)

The application of potentiometric titrations, tritium exchange, nitrogen adsorption and dissolution rates to the study of the nature of the silica and titania-aqueous electrolyte interfaces is discussed. It is shown that (1) the surface of silica could be covered with a gel layer of incompletely condensed polysilicic acid which leads to exceptionally high surface charge densities in 0.1 M KNO_3 ; (2) there is no evidence of such a gel layer or surface porosity on either heat treated silica or crystalline titania yet their surface

charge densities in 0.1 M KNO_3 were still considerably greater than predicted by classical electrical double layer theory. Therefore, it was concluded that the porous double layer theory was useful but was not a *general* explanation of the interfacial electrochemistry of metal oxides.

"Adsorbed Polymer Layers on Oxide Colloids" Brian Kavanagh (W.A.)

The adsorption of a neutral polymer, polyvinyl alcohol, on hydrated aluminium oxide (gibbsite), was studied as a function of the equilibrium solution concentration of polymer. These measurements indicated that only a very small fraction of the segments of adsorbed molecules were actually in contact with the surface of the oxide, the remainder existing in the form of loops and tails. Parallel electrophoretic mobility measurements were used to estimate the thickness of the adsorbed layer at various adsorption densities. The existence of a very thick layer of adsorbed polymer was also supported by flocculation studies.

"Analytic Theories of Steric Stabilisation" J. B. Smitham (Sydney)

Any theory of steric stabilisation should satisfy two primary requirements. These are (i) the description of the onset of flocculation in a sterically stabilised dispersion, and (ii) in stable systems, prediction of the distance dependence of the steric repulsion.

The development of a simple, analytic formula based on Flory-Huggins theory is described for the free energy of repulsion of approaching polymer coated particles.

This theory predicts a correlation between the theta point for the stabiliser chains in free solution, and the critical flocculation point of the latices. Numerous experiments on fully covered particles with well anchored stabiliser have shown this correlation exists.

Further, by the use of realistic segment density distributions for attached chains, the predictions of the distance dependence of the steric repulsion are in good agreement with the experimental evidence presently available.

"Kinetics of Emulsion Polymerization"

B. J. Hawkett (Sydney)

The kinetics of polymerization of vinyl acetate in seeded emulsion systems is considered. The theoretical equations governing the kinetics have been solved exactly (*i.e.*, without resorting to the customary steady state approximation). This permits the kinetics to be described over the entire course of the polymerization. Comparison of the predictions of the theory with the results of experiments on vinyl acetate yields information on the radical capture efficiency of the latex particles.

"Polymer Adsorption at Interfaces"

L. R. White (A.N.U.)

Some recent theoretical work on polymer conformation at a solid interface is presented. The shape of a non-interacting polymer at an interface is shown to be a function of the adsorption energy parameter W . The existence of a critical value of $W = W_c$ is demonstrated. For $W > W_c$ the polymer is adsorbed, for $W < W_c$ the polymer is desorbed. W_c is independent of the size of the polymer. Numerical calculations based on the assumption that the energy of adsorption of a monomer unit is due to dispersion forces are presented to show that the adsorption-desorption transition could be induced by raising the temperature or by increasing the refractive index of the solvent.

"Adsorption of Oleic Acid at the Goethite-Water Interface"

Robert Jung (Melbourne)

Solubility-pH diagrams as a function of concentration and ionic strength for the system oleic acid- NaNO_3 -water have been constructed from a critical review of available literature. These data have been used to help interpret adsorption and electrophoretic mobility isotherms of oleic acid on well characterized colloidal goethite. The results indicate the importance of precipitation of oleic acid species in understanding adsorption of the fatty acid as a function of pH on goethite and other surfaces. A mechanism involving coating of mineral particles by insoluble oleic acid species seems to explain much of the froth flotation of minerals by oleic acid-sodium oleate collectors.

"Coagulation of Polymer Latices"

Dr A. Homola (Melbourne)

The widespread application of synthetic polymer latices in industry and science requires that the factors and conditions affecting their stability are well understood.

An investigation of the particle-particle interaction forces, electrostatic and steric, in crowded latex systems and under well defined conditions is discussed.

The experimental techniques, such as ultracentrifugation, ultrafiltration, surface balance and compression are presented and the results analyzed in terms of the current theories of colloidal stability.

Coagulation of Colloidal Cellulose

Margaret Donnan (Melbourne)

The coagulation of the natural organic colloids produced in the manufacture of pulp and paper is of interest for the retention of fibre in the paper sheet and in clarification of water systems. These fine pulp particles are highly swollen, rich in lignin and hemicellulose, with a significant negative zeta potential.

The effect of addition of varying levels of FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 and $\text{Al}_2(\text{SO}_4)_3$ to the fibres at different pH values was discussed in terms of the effects on zeta potential and coagulation characteristics.

"Orientation of Water Molecules in the Electric Double Layer"

M. A. Habib (Flinders)

On the basis of a two state model of water molecules at electrode surfaces along with a consideration of water-water interaction, the orientational entropy was formulated and shown to pass through a maximum at a finite cathodic potential. Assuming that dimerization of adsorbed water dipoles occurs at the electrode surface, the $\Delta\chi$ potential and the dipole capacitance were calculated and it was shown that the orientation of water molecules is *not* responsible for the characteristic double layer capacitance anodic "hump" found experimentally.

"Adsorption of Surfactant and Inorganic Ions at the Dropping Mercury Electrode"

Lynne Barnett (Sydney)

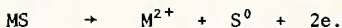
In this study of the adsorption of quaternary ammonium cations at the dropping mercury electrode, we have attempted to characterize the adsorbed layer over a wide range of surfactant and supporting electrolyte concentrations. From a thermodynamic analysis the surface excesses of the various components of the double layer were determined as functions of surfactant concentration, supporting electrolyte concentration and electrode charge.

It was found that the adsorption of surfactant cations at negative electrode charges is accompanied by a marked adsorption of bromide ions. This cooperative effect was ascribed to the formation of ion-pairs.

"The Electrokinetic Properties of Mineral Sulphides"

Michael Moignard (Melbourne)

A study of the isoelectric points of mineral sulphides using microelectrophoresis indicates that nearly all have i.e.p. values in the range pH 3-4. Supporting electrode potential studies have shown that the most likely oxidation mechanism for sulphides is through the formation of elemental sulphur, *via*, for example



The i.e.p. value for elemental sulphur itself as determined by microelectrophoresis is at pH 4. In the present paper the possibility of formation of a coating of sulphur on mineral sulphide colloids in water is discussed using ZnS as a model. It is found that an i.e.p. value different from that of elemental sulphur can be obtained only if pre-treatment conditions are kept extremely unfavourable for elemental sulphur formation.

"Slime Coating on Sulphide Minerals"

Paul Neville (Sydney)

The investigation of goethite slime coating on sulphides, in particular galena (PbS), is being treated from several different

directions.

The separate electrophoretic behaviour of galena and goethite is being followed as a function of the solution conditions, pH, ionic strength and common anion/cation concentrations.

A model system of ion-exchange resins which duplicate the electrophoretic behaviour of the two components of the slime problem, is being used to test whether hydrodynamic forces can be used to control the slime coating of say, resin A or resin B. It is hoped to be able to define a series of solution conditions and shear regimes which will effectively separate A-B interactions whilst maintaining A-A or B-B interactions. The shear regimes defined should be low enough to be used in larger operations.

Using the results from electrophoretic mobility data for goethite/galena particles it is hoped that shear regimes will be defined which will enable satisfactory separation of the slime particles from galena.

"Adsorption of Cadmium(II) at Oxide-Water Interfaces"

Pauline Stiglich (Melbourne)

Adsorption and the presence of complexing agents are two important factors affecting the presence of heavy metals in aqueous solutions. Various models of adsorption are discussed and results showing the adsorption of Cd(II) on TiO_2 and $FeOOH$, as a function of pH are presented.

Results are qualitatively analysed in terms of the various hydroxy species in solution. These results indicate that the uptake of metal ions by the surfaces, parallels the increase in the hydroxy species, $Cd(OH)^+$ and $Cd(OH)_2^0$ in solution. Thus these hydroxy complexes appear to be important species involved in adsorption.

"The Charge Behaviour of Kaolinite" Michael Boland (West Australia)

The charge behaviour of seven natural kaolinities was studied using an exchange technique. The kaolinities were found to possess both positive and negative surface charge. The positive charge was found to increase with a decrease in pH of the aqueous suspension and

with an increase in the ionic strength of the medium. It was concluded that the positive charges are a result of the protonation of surface exposed alumina. The negative and net charge was found to be almost pH-independent in the pH range 3.5 to 8.5 when soluble aluminium was taken into account. The negative charge was concluded to be a result of isomorphous substitution together with some pH-dependent negative charge due to surface exposed silica.

"Electron Microscopic Techniques in the Study of Colloidal Dispersions"

Richard Green (West Australia)

Preparation techniques have been developed for the electron microscopic examination of a range of colloidal dispersions. Fine clay particles and flocs were adsorbed from an upright drop of suspension onto positively charged films (Cytochrome C) on carbon coated support grids. The excess suspension was removed by washing the grids in ethanol. The natural negative charge of the carbon coated grid was used for ferric polycations and precipitates. Large, thick particles such as clay aggregates were examined by adsorbing them onto a charged film from an inverted drop of suspension and then preparing a replica of their surfaces. A one-stage replica technique was modified to study the acid dissolution of crystals of goethite and hydroxyapatite. The crystals were only partly dissolved from the replicas and the crystal residue was then examined lying within the replica of the original crystal. Selective dissolution of lime and then clay from replicated aggregates was used to study the composition of aggregates formed by the interaction between saturated lime and particles of Ca-illite.

Freeze etching and embedding techniques were described as possible methods of examining the structure of flocs formed in suspension.

"Hydrolysis and Precipitation of Aluminium(III)"

Elizabeth Bate (Melbourne)

An investigation of the aqueous chemistry of Al(III) was undertaken in an attempt to gain information about the hydrolysis

products of aluminium and to determine the morphology of the precipitants.

Ageing experiments show that equilibrium was only slowly achieved; the concentration of the monomeric species of aluminium remained essentially constant; however, the polymeric species, determined to be $Al_8(OH)_{20}^{4+}$, was converted to solid aluminium hydroxide with ageing.

The crystalline structures of the precipitates were identified by electron microscopy and by X-Ray diffraction measurements, to be gibbsite at acidic pH, and bayerite at alkaline pH.

"Photochemical Reactions on Semiconductors"

Alan Durbridge (Melbourne)

The paper concerns the photochemical redox reactions which occur on the surface of a semiconductor, under the influence of U.V. irradiation. The semiconductors considered were ZnS and TiO_2 , the redox reactions being the oxidation of potassium ethyl xanthate and the reduction of oxygen. Particular emphasis is placed upon the rates of reaction under changing conditions of xanthate and solid concentrations. The ultimate aim is to propose a mechanism for the adsorption and subsequent oxidation of xanthate from the kinetic results obtained from both solids.

"The Surface Chemistry of Amosite Asbestos"

John Ralston (Melbourne)

The purpose of this project was to study the surface characteristics of the complex amphibole silicate, amosite in relation to its behaviour in aqueous solution. It is hoped that the results obtained in this investigation will serve both as a useful model for predicting the flotation characteristics of amphibole minerals in mineral flotation systems and, at the same time, aid future research work directed towards the eradication of lung disease where various forms of asbestos have been shown to be connected with the development of asbestosis and mesothelioma.

The leaching of amosite has been studied as a function of pH

in the range 4 to 10 and at 25, 35 and 45 °C. These studies, combined with an investigation of the mineral's ion exchange properties, have revealed that a residual, negatively charged silicate layer prevents deep penetration of reagents into the amosite lattice. Contact angle studies have shown that there are no detectable intrinsic cation activators on the leached amosite surface, whereas cationic collectors of the type $RN(CH_3)_3^+$ are readily adsorbed. Both contact angle and adsorption measurements indicate that the amount of cationic collector adsorbed increases with pH. A zeta potential study has shown that there is a close similarity between the nature of amosite and quartz surfaces in aqueous solution; the amosite surface bears an increasingly negative charge as the pH increases. Adsorption of cationic collector causes the zeta potential to be reversed in sign at a point where available negative surface sites have been occupied by long chain cations. It has been noted in this investigation that trace amounts of intrinsic inorganic and organic impurities can influence the leaching and flotation behaviour of amosite.