

TENTH
AUSTRALIAN COLLOID AND SURFACE CHEMISTRY
STUDENT CONFERENCE

UNIVERSITY OF MELBOURNE
(MT. ELIZA VIC.)

1982



Big fleas have little fleas
Upon their backs to bite 'em
And little fleas have littler fleas
And so, ad infinitum.

PROCEEDINGS AND ABSTRACTS
OF THE TENTH
AUSTRALIAN COLLOID AND SURFACE CHEMISTRY
STUDENT CONFERENCE
UNIVERSITY OF MELBOURNE, 1982

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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, however, also provided by generous donations by: The Potter Foundation (G.E. Alexander Fund); Dulux (Australia); Catoleum; CSIRO; Australian Mining and Smelting; ICI; Unilever; James Hardie; Tioxide (Australia); 2nd Australian Rheology Conference; and Alex Boden. The ANU and the Universities of Sydney and Melbourne also made significant contributions to the overall running costs.

All concerned with the meeting thank these sponsors for making this and other Australian Colloid Student Conferences possible. The participants also wish to thank their Melbourne hosts and especially the Conference Secretary, Mr. Robert Lamb for the effort put into making the meeting the success it undoubtedly was.

PREFACE

The 10th Australian Colloid & Surface Chemistry Student Conference was held in Melbourne, February 1982. The Abstracts that follow were prepared by the postgraduate students from the Universities of Melbourne Sydney, ANU, NSW, Monash together with Bendigo and Pharmacy Colleges of Victoria and the Royal Melbourne, Swinburne and S.A. Institutes, who presented papers at the conference.

The first two conferences in Sydney and Melbourne established the atmosphere and motivation for all subsequent gatherings. Students presented papers on their own research to an audience of their peers, their immediate supervisors, other local and overseas academics and visitors from Australian Government and Industrial Research Centres. Bob Hunter and I, as originators of these conferences, perceive a general increase in excellence and in the standard of presentation, due no doubt in part to our advancing age! It is also a manifestation of success of the teaching role of each conference as well as an acknowledgement of the steady rise to international leadership of the Australian Colloid Science Community.

It is proper then to celebrate this 10th Anniversary and to acknowledge the achievements of the current group of students and of all alumni of these unique gatherings. We also celebrate the achievements of the several groups around the country; from outside the nation, we are seen as a single group. Such coherence is fostered by our student conferences where inter and intra group teaching, debate and competition are sensibly balanced.

It is also a time to reflect on the prospects of the next 10 conferences as Australian science in Universities, Government research labs and industrial centres feels the cuts made to our activities. It is relatively easy for Colloid Scientists to justify their existence in terms of relevance and short

term research. Colloid science is important in enhanced oil recovery, it is central to fine mineral processing, it is making contributions to our understanding of nutrient availability in soils or in the control of heavy metal pollution of our waterways. But short term success is illusory each of us knows that our answers to such immediate problems are at best qualitative. I suggest that we, of all scientists, have a duty to argue with our sponsors for support of long term research on the fundamentals of particle-particle interaction in colloidal systems, or for support for studies of the molecular processes at electrodes or of the structure of water at interfaces and on and on. Without such basic work, applied science will work in a vacuum.

Our Colloid and Surface Chemistry Students Conferences owe their success to the energy and enthusiasm of the participants, and to the sponsors - Universities, CAE's, CSIRO and Industrial groups - who each time give to keep this unique conference alive. We also need to acknowledge the ten secretaries, all students, who have organized the detailed programme and provisions. From one to ten the secretaries were John Hayter (Sydney), Bob James (Melbourne), Harley Wright (Sydney), David Yates (Melbourne), Bruce Firth (Sydney), Joe Woolfe (ANU), John Lyons (Melbourne), Col Bensley (Sydney), Steve Carney (ANU) and Rob Lamb (Melbourne). To all of them from all of us - thank you.

Tom Healy,

Melbourne 1982.

PARTICIPANTS - 1982

Guest of Honour

Professor D. Tabor (Cambridge University)

From the University of MelbourneStaff

Professor T.W. Healy
 Dr. F. Grieser
 Dr. L. White
 H. Oshima
 Dr. J. Lane
 P. Butler
 P. Freeman
 L. Cruickshank

Students

J. Aston
 C. Drummond
 D. Dunstan
 I. Harding
 S. Heard
 R. Lamb
 B. Lovelock
 A. Lau
 I. Metcalfe
 G. Warr

From the University of SydneyStaff

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 Dr. R. Gilbert
 Dr. H. Flitt

Students

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 B. Chamberlain
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 N. Ekdawi
 J. Feeny

From the Australian National UniversityStaff

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 G. Rose
 M. Redwood
 Dr. D. Atkinson
 G. Newcombe
 P. Scales

Students

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 P. Blake
 W. Kent

From the Victorian College of Pharmacy

Dr. R. Oppenheim
 E. Gibbs (student)
 K. Kennedy (student)

From the Royal Melbourne Institute of Technology

P. Daivis (student)

From the Bendigo Institute of Technology

B. Johnson
 J. McLelland (student)

From the South Australian Institute of Technology

K. Quast

From the University of New South Wales

Dr. R. O'Brien (staff)
 W. Perrins (student)
 A. Suki (student)

From Monash University

R. Mills (student)

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VISITORS

From CSIRO (Applied Organic)

Dr. D.N. Furlong

Dr. Y. Tricot

From CSIRO (Canberra)

C. James

From CSIRO (Food Research)

Dr. L. Fisher

From Department of Defence (Materials Research)

D. Williams

From Rockwell Corporation, U.S.A.

Mr. Ora Smith

Dr. Bernard Titmann

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Dulux (Australia) Limited

J. Rainbow

ICI (ANZ)

Dr. D. Fenson

10th AUSTRALIAN COLLOID AND SURFACE CHEMISTRY
STUDENT CONFERENCE 1982

PROGRAMME

Venue: Camp Manyung, Mt. Eliza, Victoria

Thursday, February 11, 1982

12.00 noon	REGISTRATION	
12.30 p.m.	LUNCH	
2.00 p.m.	OPENING COMMENTS	
2.15 p.m.	"Formation of Microscopic Liquid Bridges between Surfaces"	Hugo Christenson (ANU)
2.40 p.m.	"E.S.R. Spectroscopic Studies of Polymerization Reactions"	Matt Ballard (Sydney)
3.05 p.m.	"Bubble Size and Changing Contact Angles on Plastic Surfaces"	Robert Lamb (Melbourne)
3.30 p.m.	COFFEE/TEA	
3.45 p.m.	"Polymerization within Emulsion Droplets"	Bruce Chamberlain (Sydney)
4.10 p.m.	"A Theoretical and Experimental Treatment of 'Wall Effects' in Du Noüy Ring Tensiometry"	Ian Metcalfe & Pam Freeman (Melbourne)
4.35 p.m.	"Elastic Properties of Coagulated Colloidal Dispersions"	Dr. H. Flitt (Sydney)
5.30 p.m.	DINNER	

Friday, February 12, 1982

9.00 a.m.	"A Spectroscopic Study of Ionizable Monolayers"	Brendon Lovelock (Melbourne)
9.25 a.m.	"Emulsions and Fine Particles Recovery"	Warren Kent (Swinburne)
9.50 a.m.	"Adsorption of Cadmium(II) onto Hydrophobic Surfaces"	Alice Lau (Melbourne)
10.15 a.m.	"Charge Effects in Emulsion Polymerization of Styrene"	Ian Penboss (Sydney)
10.40 a.m.	COFFEE/TEA	
10.55 a.m.	"Aggregation of Quaternary Ammonium Bromides with Two Long Alkyl Chains"	Lindsay Angel (ANU)

11.20 a.m.	"Effect of pH and Ion Concentration on the Ultrafiltration of Protein Solutions using Artificial Membranes"	Anhar Suki (NSW)
11.45 a.m.	"Surface Enhanced Raman Studies on Au and Ag Colloids"	Sue Heard (Melbourne)
12.10 p.m.	LUNCH	
2.00 p.m.	"Continuous Molecular Weight Distribution from Photon Correlation Spectroscopy"	Peter Daivis (RMIT)
2.25 p.m.	"The Aqueous Chemistry of Polydisperse Non-Ionic Surfactants"	Greg Warr (Melbourne)
2.50 p.m.	"Packing of Amphiphile Chains in Micelles"	Emma DeLacey (ANU)
3.15 p.m.	"Physical Characterization of some Microporous Carbons by Adsorption of Gases, Vapours and Liquids"	Dr. D. Atkinson (Swinburne)
3.40 p.m.	"Surface Chemistry Studies of Kevlar-49"	Daryl Williams (Defence Dept)

Students Vs Others

CRICKET MATCH

B.B.Q DINNER

Saturday, February 13, 1982

9.00 a.m.	"Manufacture and Testing of Triamcinolone Acetonide Nanoparticles"	Karen Kennedy (Vic Pharmacy Col)
9.25 a.m.	"Using Nanoparticles to Target Drugs"	Elizabeth Gipps (Vic Pharmacy Col)
9.50 a.m.	"Controlled Tailoring of Quartz Surfaces and its Relation to Collectorless Flotation"	Peter Blake (Swinburne)
10.15 a.m.	"Electrical Conductivity of Colloidal Dispersions at Low Frequency"	Lucy Muchic (Sydney)
10.40 a.m.	COFFEE/TEA	
10.55 a.m.	"Calorimetric Studies of Some Non-Ionic Surfactants"	Jeff Aston (Melbourne)
11.20 a.m.	"The Structure of Strongly Interacting Colloidal Systems"	Brian Beresford-Smith (ANU)
11.45 a.m.	"Chemically Modified Lignins - their Purification and Interaction with Solid Surfaces"	Veronica Nyman (Swinburne)
12.10 p.m.	LUNCH	

2.00 p.m.	"Adsorption of Cadmium(II) on Zwitter-ionic (amphoteric) Latices"	Ian Harding (Melbourne)
2.25 p.m.	"Statistical Mechanics of Polar Fluids"	Glen Walker (ANU)
2.50 p.m.	"Competitive Adsorption of Cobalt and Copper on Goethite"	John McLelland (Bendigo CAE)
3.15 p.m.	"The Wettability of Hydrophobic/hydrophilic Surfaces in the Presence of Non-Ionic Surfactants"	Peter Scales (Melbourne)
3.40 p.m.	COFFEE/TEA	
3.55 p.m.	"Effects of Spatially Varying Polarization in Ice and Aqueous Solution"	Dr. D. Gruen (ANU)
4.20 p.m.	"The Depression of Arsenic Minerals in the Flotation of Broken Hill Lead Concentrates"	Keith Quast (S.A.)
4.35 p.m.	"Crystallization Studies in Waxy Crude Oil: the Role of Polymer Inhibitors"	Russell Mills (Monash)

ABSTRACTS

Formation of Microscopic Liquid Bridges Between Surfaces

H.K. Christenson (ANU)

The effect of small amounts of dissolved water (up to saturation) on the forces between mica surfaces in non-polar organic liquids has been investigated. The oscillatory force curve exhibited by most dry liquids is drastically changed by the presence of only moderate amounts of water. The oscillations diminish in range and amplitude and are eventually, at high water concentrations, swamped by very large attractive forces. The condensation of bulk water between two mica surfaces in or very close to contact is observed well before saturation of the liquids with water is attained. This phenomenon is a manifestation of Kelvin condensation, analogous to that encountered in condensation from undersaturated vapour.

Electron Spin Resonance Studies of Polymerization Reactions

M.J. Ballard, D.H. Napper, R.G. Gilbert and P. Pomeroy (Sydney)

The spectra of propagating free radicals have been obtained previously.¹ However, this could only be done under extremely unusual initiating conditions, only in the first five percent or so of the reaction, and never in emulsion-type systems. As well, no useful kinetic information was obtained. In recent work, we have been able to obtain time-dependent spectra of the methyl methacrylate propagating free radical, under ordinary (i.e., industrial) initiating conditions, in an emulsion system. Useful kinetic information has been obtained, both quantitative and qualitative. Further work will enable the determination of absolute radical concentrations.

¹ Smith & Stevens, (1972) J. Phys. Chem., 76, p.3141-3151

Bubble Size and Changing Contact Angles on Plastic Surfaces

R. Lamb (Melbourne)

The independence of contact angle with drop size has been accepted, with some exceptions, by the majority of workers for many

years. Recently, however R. Good and M. Koo* have questioned this approach, suggesting that contact angle dependency is more widespread than initially believed. For the systems water/polymethylmethacrylate and water/Teflon FEP they have shown a marked decrease in contact angle with drop sizes below 3 mm base diameter. A critical evaluation of methods and materials for the latter was made.

Measurement of contact angles was not significantly hindered by the use of a relatively large needle in the smaller drops. However reduction of possible airborne contamination by utilizing air bubbles rather than water drops produced virtually no size effect. Pretreatment of the solid surface to reduce roughness (i.e., polishing, pressing etc.) and external contamination (washing) was assessed. Chemical characterization of this surface, on the other hand was difficult, due to the proprietary nature of the material. A novel method was developed to reduce variables such as additives (e.g., plasticizers) and by-products (e.g., surfactants) to a minimum. This was achieved by strong surface oxidation using gaseous fluorine at 150 °C.

A reproducible Teflon FEP surface (from contact angle measurement) was produced which was independent of the origin of the material. Good and Koo's subsequent analysis of their experimental results was dependent upon a small degree of surface heterogeneity. The introduction of F₂ treatment in similar experiments removes this but a small effect (attributed to an enhanced water contamination effect in small drops) is still evident.

* R.J. Good and M.N. Koo, J. Col. Int. Sci (1979) 71 283.

Polymerization within Emulsion Drops

Bruce Chamberlain (Sydney)

The conditions necessary for polymerization to occur within emulsion droplets were discussed. Ugelstad and co-workers have claimed that an emulsion system stabilized with a long chain alcohol did polymerize within the droplets, however the proof of this

occurring was inconclusive. The kinetics and particle size distributions of this system were studied to establish the actual locus of polymerization. The kinetics were modelled which showed that the rate of entry into droplets was lower than entry into polymer particles under identical conditions. This explains why the rate of polymerization in such systems is relatively slow. One possible explanation for this low capture efficiency could be the difficulty of displacement of surfactant molecules by the incoming oligomeric free radicals.

A Theoretical and Experimental Treatment of 'Wall Effects' in Du Noüy Ring Tensiometry

Ian Metcalfe and Pam Freeman (Melbourne)

A rigorous theory of du Noüy ring tensiometry has been developed to calculate the surface tension (γ_{ab}), of a liquid with infinite or finite interfaces. A computational algorithm has been written to calculate the magnitude of these 'wall effects' and evaluate f_{corr}^{wall} , the wall correction factor.

Experiments were carried out on both hydrophilic, glass cylindrical walls and hydrophobic wax coated containers (contact angles 0° and 105° respectively) and for a number of wall to ring radii ratios (W/R).

A graph of the theoretical parameter ratio, $f_{corr}^\infty / f_{corr}^{wall}$, (where f_{corr}^∞ is the infinite interface correction factor) and the experimental equivalent M^∞ / M^{wall} (where M is the maximum mass measured) vs. W/R shows impressive agreement.

The surface tension of a liquid measured in a walled container is given by:

$$\gamma_{AB} = M^{wall} g / 4\pi R f_{corr}^{wall}$$

The use of the above formula and the computer program to give the correction factors allows accurate surface tension measurements to be made in cylindrical containers.

Viscoelastic Properties of Coagulated Sols

Dr. H. Flitt (Sydney)

The flow behaviour of coagulated sols has been explained by "the elastic floc" model developed by Hunter and coworkers. Contributions to energy dissipation are of a viscous nature plus the elastic energy required to stretch bonds between particles. Viscous energy dissipation is due to external fluid flow around flocs and internal fluid movement inside flocs, during floc collisions. It was proven that the latter viscous contribution could account for flow behaviour, as the first was insignificant. The elastic energy dissipation was even more insignificant than the two viscous mechanisms of energy dissipation. Hence to measure the elastic response of coagulated sols a very sensitive dynamic rheometer has been developed to measure dynamic rigidity G in the order of $10^{-1} - 10^{-3} \text{ N m}^{-2}$ which is the range of G predicted from the elastic floc model. Basic design of the instrument is a hollow cylinder which oscillates on a torsion wire suspended in a concentric annular ring.

Recent experimental studies on coagulated sols have examined the relationship of G as a function of zeta potential ζ . The elastic floc model suggests a squared relation of ζ with G and this is found experimentally at small degrees of coagulation (high ζ). However the problem of network structures (gels) forming at high coagulation (low ζ) tends to make measurements of G inaccurate. The aim of this study is to determine the nature of the primary minimum of the particle-particle interactions made from DLVO theory and a short range Born repulsion force.

A Spectroscopic Study of Ionizable Monolayers

Brendon Lovelock (Melbourne)

The dissociation constant of an ionizing group bound to a solid/electrolyte interface is a function of two major variables. Firstly, the dielectric environment of the group and secondly the potential it experiences from the ionization of surrounding groups. If the effect of potential can be isolated from the dielectric

effect, then the change in pK can be used to measure the potential at the surface where the ionizing group resides. The pK of a surface may be determined directly if the charged group has a change in its absorption or fluorescence spectra upon ionization. In the experiments presented, the applicability of the fluorescence probe octadecyloxynaphthoic acid, to the study of potential on flat plate and micelle systems was investigated.

Emulsions and Fine Particle Recovery

Warren Kent (Swinburne)

The general importance of fine particles in the initial mineral concentration by froth flotation is considered. Problems associated with fines and a brief discussion of methods for their recovery is presented. A novel system for fines recovery using selective, polymer stabilized oil droplets to form robust mineral particle - oil droplet aggregates is then presented; including experimental results and proposed future investigations.

Adsorption of Hydrolysable Cd(II) onto Hydrophobic Surfaces

Alice Lau (Melbourne)

A reliable method was developed for dispersing highly hydrophobic materials in aqueous solutions. The solids chosen were naturally hydrophobic carbon black and carbon black graphitized at 1500 °C and 2700 °C. These substrates were characterized using techniques of nitrogen adsorption, microelectrophoresis, and partitioning between water and hexane.

The adsorption behaviour of Cadmium(II) on these hydrophobic surfaces was studied as a function of pH.

A comparison was made between the adsorption on hydrophobic materials and a hydrophilic, hydrous metal oxide SiO₂. Adsorption phenomena were found to be different between the two types of substrates. This may result from the relatively high hydrophobicity of carbon black surfaces, or may be due to the presence of different types of adsorption sites on carbon black, as compared with SiO₂.

Charge Effects in the Emulsion Polymerization Kinetics of Styrene

Ian Penboss (Sydney)

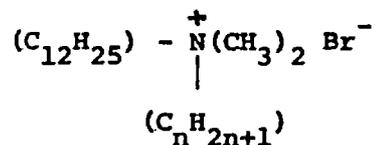
The present state of theoretical and experimental understanding of emulsion polymerization kinetics of styrene now allows the experimental determination of such kinetic parameters as entry and exit of free radicals into and out of polymer latex particles. Previous investigations had used anionically stabilized systems with potassium persulfate as initiator. The present work examined the effects on the polymerization process when initiated with alternative initiator systems. Particular attention was paid to any charge effects going from the negative sulfate radicals to uncharged hydroxyl radicals and positively charged organic radicals.

It was found that a hydrogen peroxide - iron(II) sulfate system provided entry rate coefficients similar to persulfate systems thus implying that charge is not a major contributor to the entry process. Slight increases in exit rates were attributed to ferric ions acting as chain transfer agents. Cationically initiated systems showed significant deviations from the theory due to probable surface charge density effects.

Aggregation of Quaternary Ammonium Bromides with Two Long Alkyl Chains

Lindsay Angel (ANU)

A series of quaternary ammonium bromides - general structural formula



has been prepared and the self aggregation of these compounds in aqueous solution investigated using conductivity and light scattering techniques.

In aqueous solution at ambient temperatures ($t \sim 25^\circ\text{C}$) it has been shown that the surfactants aggregate to form micelles when $n \leq 8$, while bilayers are formed for $n \geq 10$. This behaviour is interpreted in terms of the Israelachvili, Mitchell, Ninham theory of amphiphile

aggregation, and within the framework of this theory the transition around $n = 9$ has allowed for the estimation of various relevant parameters for the aggregates, and to some extent the prediction of the aggregate geometry formed by a given member of the series.

Some relevant free energy of transfer data will also be discussed.

The Effect of pH and Ionic Concentration on the Ultrafiltration of Protein Solutions using Artificial Membranes

Anhar Suki (NSW)

This paper discusses the ultrafiltration (UF) of protein (BSA) solutions with retentive membranes over a range of pH values (2 to 10) and concentrations of salt. For fixed feed concentration the flux declined at all conditions. The final UF flux was found to correlate with the amount of protein adsorbed onto the membrane, particularly when salts were absent. Adsorbed protein was found to be greater following the UF of BSA in salt solutions, and maximum adsorption occurred at the iso-electric/iso-ionic points. Initial and long-term fluxes varied with pH. A flux minimum occurred at the iso-ionic point in the absence of salts, but in the presence of 0.2M NaCl the flux was a minimum at pH 2.0 and increased monotonically with pH. In general flux in the absence of salts was greater than in salt solution, except around the iso-electric point (\approx pH 5), where the presence of salt gave a significantly higher flux. These observations were supported by measuring UF flux transients following a step input of salt, which produced flux drops at pH 2 and 10, but flux increase at pH 5. The results are explained in terms of the effect of different ionic environments on the permeability of the adsorbed protein and the membrane. Conformational changes and charge properties of the BSA appear to be the dominant factors determining the flux.

Surface-Enhanced Raman Studies on Ag and Au Colloids

Sue Heard (Melbourne)

The anomalously large Raman signal intensities of molecules

adsorbed on certain metal surfaces (e.g., Ag, Au) is the key observation in the study referred to as Surface-Enhanced Raman Spectroscopy (SERS). Other observations and some models proposed for this effect are briefly discussed.

Silver and gold colloids as substrates which support SERS have been studied using electron microscopy and visible absorption spectroscopy. The sols are seen to consist of multiply-twinned, pentagonal biprismatic particles which, upon addition of adsorbate, form non-coalescing aggregates.

Orientation studies of 4-dimethylaminopyridine adsorbed on a Ag sol by comparison of relative band intensities in the solution and SER spectra support attachment to the surface through the pyridine ring end of the molecule.

Continuous Molecular Weight Distributions from Photon Correlation Spectroscopy

Peter Daivis (RMIT)

Photon correlation spectroscopy has gained wide acceptance as a means of measurement of the diffusion coefficient for dissolved macromolecules. The determination of molecular weight and polydispersity from PCS measurements has been a problem to which many authors have addressed themselves over the years.

Most commonly the method of cumulants due to Köppell has been used with some success. Recently, however, techniques of data analysis which are capable of extracting the maximum possible resolution from PCS data have been proposed by Provencher and Pike and McWhirter, independently.

The method of Provencher, known as constrained regularization is discussed and some results using synthetic and real data are presented.

In brief summary, it can be said that Provencher's computer program gives good results for unimodal distributions with M_w/M_n up to 2.00 without great difficulty, but bimodal pose some problems. With more suitable data, it is possible that bimodal distributions may also be obtained.

The Aqueous Solution Chemistry of Polydisperse Nonionic Surfactants
Gregory Warr (Melbourne)

A simple model for the micellization of ideal surfactant mixtures is developed using a phase separation model. This is used to predict the critical micelle concentration of mixtures, the concentration of monomeric surfactant species in solution, and the average composition of the micelles as a function of total concentration.

Experimental verification of the theory for two polydisperse polyoxyethylene nonylphenol surfactants was obtained by ultrafiltration of submicellar and micellar solutions. Excellent agreement between theory and experiment was observed in both of the systems studied.

Packing of Amphiphile Chains in Micelles

Emma de Lacey

A statistical mechanical model for the packing of amphiphile chains in micelles is described. All conformations of a single chain are generated. The results of experiments on bulk liquid alkane give the kinking energy for the chains. No water is allowed into the hydrophobic core of the micelle and the chains are forced to pack at liquid hydrocarbon density throughout the core.

Results show that the chains in micelles are very disordered and only slightly less kinked than in bulk liquid alkane. Furthermore, all segments of the chains sample the surface of the micelle, bringing them into contact with water. This means that it is unnecessary to invoke the theoretically dubious idea of water penetration into micelles in order to explain experimental results which suggest hydrocarbon - water contact.

Physical Characterisation of Some Microporous Carbons by

Adsorption of Gases, Vapours and Liquids

Dianne Atkinson (Swinburne)

Adsorption isotherm measurements, Calvet immersion

microcalorimetry, and continuous addition adsorption microcalorimetry were used to characterise the microporous nature of the carbons, AMOCO PX21 and a charcoal cloth AM/4. Comparison was made with Vulcan 3G as a standard non-porous carbon.

Nitrogen adsorption isotherms (Type I) indicated a very small external surface (< 1 %) and no hysteresis associated with capillary condensation in mesopores (20 - 200 nm). A micropore filling mechanism explains best the adsorption process in these carbons. Vulcan 3G displayed Type II isotherms consistent with layer by layer adsorption. The AMOCO carbon exhibited an unrealistic BET 'apparent surface area' of $3700 \text{ m}^2 \text{ g}^{-1}$ and a second linear region of the N_2 adsorption isotherm below p/p_0 0.2 associated with an enhanced uptake. For toluene adsorption this feature was not present and was explained as filling of slightly larger micropores up to 2 nm in diameter (termed 'secondary micropores'). The charcoal cloth ($1250 \text{ m}^2 \text{ g}^{-1}$) did not contain these extra micropores, only those with diameters up to 1 nm. Water adsorption (Type V isotherms) indicated the non-specific nature of these carbons, lacking surface functional groups.

Heat of immersion studies using a series of 'molecular probes'; toluene, mesitylene, isodurene, *n*-hexane, neohexane and cyclohexane, highlighted the failure of referring to the BET 'surface area' in microporous systems. A thermodynamically-sound reference would be the capacity of each microporous solid for each immersion liquid and thus an integral heat of adsorption may be calculated. Trends with size and shape of the liquid molecule indicated narrower slit-like pores in the charcoal cloth whereas a more open, wider pore system was evident for the AMOCO carbon.

Differential heats of adsorption as a function of volume-filled were obtained for nitrogen and argon adsorption by the continuous addition method. Enhancement of the heat (to 12 - 14 kJ mol^{-1}) occurred only at very low uptake, after which they decreased gradually to the level of condensation. The AMOCO carbon featured a small plateau at about 9 kJ mol^{-1} corresponding only to 50 % primary micropore filling rather than the start of secondary micropore filling. The enthalpic and entropic features of the enhanced uptake in these secondary micropores are still being discussed.

Wettability of Kevlar 49

Daryl Williams (Defence Department)

Contact angles have been measured on Kevlar 49 fibres, an aromatic polyamide, using Carroll's drop profile method. The surface free energy, γ_{SV} , has been estimated for Kevlar 49 and recalculated for Nylons using Wu's method. The relationship between the orientation of intra-planar hydrogen bonding and surface energy for polyamides is discussed. Initial attempts to modify the wettability of Kevlar 49 have yielded encouraging results.

Manufacture and Testing of Triamcinolone Acetonide Nanoparticles

Karen Kennedy (Victorian Pharmacy College)

Rheumatoid arthritis is a prevalent and painful disease. In its early stages it presents as an acute inflammation of the affected joint. This results in the infiltration of large numbers of phagocytic cells into the joint. Amongst other things these cells secrete lysosomal enzymes which contribute to joint damage.

The current treatment of the disease is inefficient in that insufficient drug gets to the site of action, the remainder causes unwanted side effects and the patients often prefer to put up with the disease rather than take their medicine.

In an attempt to overcome these problems we have been using, in conjunction with E.R. Squibb & Sons, anti-inflammatory steroids coupled to a colloidal carrier. This drug delivery system is then injected into the affected joint where it is engulfed by the phagocytic cells and the enzyme release inhibited. The nanoparticles cannot escape from the joint into the general circulation to cause adverse reactions.

A sub-micron cross-linked albumin particle containing triamcinolone acetonide is made using a coacervation-like technique. Although the poor aqueous solubility of the drug limits the payload of the system to under 1 %, the drug is very potent and so only small amounts are needed for effective action.

Early biochemical testing of the product using polymorph cells shows that it could inhibit the release of a proteoglycanase enzyme thought to be implicated in cartilage degeneration.

Future work will involve using the triamcinolone acetonide nanoparticles in a whole animal model of rheumatoid arthritis. A more water soluble salt of triamcinolone acetonide will also be incorporated and tested.

Using Nanoparticles to Target Drugs

Elizabeth Gipps (Victorian Pharmacy College)

Anti-cancer drugs affect both cancer and normal tissue. To get the best from anti-cancer drugs a high concentration is needed in the cancer. To decrease side-effects a low concentration is needed elsewhere. To achieve this aim the drug may be given by regional perfusion, or by linking to an anti-tumour antibody, or some other carrier. The carriers that have been used include DNA, liposomes, and micro and nano-sized particles made from synthetic polymers or albumin.

The carrier we have been using is a cross-linked albumin particle made by a coacervation-like technique. With these we have achieved a 7 % payload of the drug, 5-Fluorouracil, in the particles. When tested in vitro against B16 mouse melanoma and mouse mammary virus tumour the nanoparticles delay growth and decrease the growth rate of the tumour. When the Fluorouracil nanoparticles are used to treat the B16 melanoma in C57BL/6 mice the increase in survival time is approximately equal to that obtained with treatment with free Fluorouracil.

Controlled Tailoring of Quartz Surfaces with Relation to Natural Flotation

Peter Blake (Swinburne)

Minerals are conventionally floated in the froth flotation process by selectively adsorbing organic species at the solid-water interface, thus conferring hydrophobicity onto the solid surface, with the result that air bubbles can then attach them-

selves to the mineral surface. The aggregates of particles and air bubbles are then removed as a froth at the top of a flotation cell.

Recent studies have shown that chalcopyrite and sphalerite may, under certain conditions, be floated in the absence of collector.

In the investigation of naturally floatable materials, the surface of quartz has been prepared with varying degrees of hydrophobicity. Thus, as the hydroxyl groups of the quartz surface are replaced by covalently-bonded methylsilyl groups, a normally hydrophilic surface ($\theta = 0$) is converted to one that is successively more hydrophobic ($\theta \gg 90^\circ$).

Thus with a model mineral system one is able to ascertain the surface coverage of hydrophobic centres that leads to a given rate of flotation at a given particle size.

Electrical Conductivity of Colloidal Dispersions at Low Frequency

Lucy Muchic (Sydney)

The systems studied in this work were dilute suspensions of monodisperse polystyrene, satisfying the requirements of small ϕ , small ka and small a . The electrical conductivities of these characterized latices have been measured, at low frequency. The effect of varying the electrolyte and ionic strength have been investigated, for a range of ka values. Various methods of determining the conductivity of the suspending medium were explored. Experimental values and theoretical values have been obtained for the conductivity increment $\left[\left(\frac{K^*}{K^\infty} - 1 \right) / \phi \right]^1$, using O'Brien's theory.² These were used to test and establish the limits of the theory. From the results, inadequacies in the theory have been detected.

1. K^* - conductivity of the suspension
 K^∞ - conductivity of the bulk electrolyte
 ϕ - volume fraction of particles.

2. O'Brien, R.W., J. Coll. Interf. Sci., 81, 234 (1981).

A Calorimetric Study of the Adsorption of some Nonionic Surfactants
Jeff Aston (Melbourne)

Polyoxyethylene nonylphenol surfactants are polydisperse mixtures of molecules with varying numbers of "hydrophilic" ethylene oxide groups per nonylphenol "hydrophobe". These mixtures are distributed about a mean molecular weight (a mean number of ethylene oxide groups per nonyl phenol, N) according to a Poisson distribution.

Adsorption of one such surfactant, N9, onto solids of increasing "hydrophobicity", i.e., silica, surface methylated silica, surface butylated silica and graphitized carbon gives isotherms that reflect the relative surface "hydrophobicity".

Langmuir isotherms are observed with the "hydrophobic" surfaces whereas an S-shaped isotherm, convex to the concentration axis, is observed with the "hydrophilic" silica surface. The surfactant is observed to have less affinity for the silica surface than for surfaces for which Langmuir isotherms were obtained. The surfactant affinity for the surface is observed to increase with methylated silica and even more affinity for the surface is observed with graphitized carbon and the butylated silicon.

Standard free energies of adsorption, $\Delta G_{\text{ads}}^{\circ}$ obtained from the Langmuir adsorption isotherm by extrapolating to zero concentration reflects this increasing affinity for the hydrophobic surfaces. Values of, -12 kJ/mol of adsorbed surfactant for methylated silica and -30 kJ/mol for both the graphitized carbon and butylated silica.

Calorimetric experiments using the technique of flow microcalorimetry have enabled the direct measurement of the enthalpy ΔH_{ads} of adsorption of N9 onto hydrophilic silica surfaces. A value of approximately -6 kJ/mol has been obtained.

The Structure of a Strongly Interacting Colloidal System

Bryan Beresford-Smith (ANU)

Dilute aqueous dispersions of charged polystyrene spheres can show considerable short range order reminiscent of the ordering in simple fluids. Brown *et al.* (1) probed this structure using conventional light scattering techniques. Predictions of their results using liquid state theory are examined.

Monte Carlo methods using an effective DLVO pair potential have been applied to the system by van Megen and Snook (2). It is shown that their results are close to those obtained by using a conventional one-component plasma model.

Finally, a highly asymmetric electrolyte model has been solved using integral equation methods and the Hypernetted Chain Approximation. This model should contain all the essential physics of the system and some preliminary results are demonstrated.

(1) Brown, J.C., Pusey, P.N., Goodwin, J.W., and Ottewill, R.H., *J. Phys. A*, 8, 664 (1975).

(2) van Megen, W., and Snook, I., *J. Chem. Phys.*, 66, 813 (1977).

Chemically Modified Lignins - their Purification and Adsorption onto Solid Surfaces

Veronika Nyman (Swinburne)

Due to the problems of disposal of paper pulping waste, extensive research in this area is required. In particular, studies on the behaviour of lignins, which give rise to the black colour of the effluent are required.

Preliminary work on unfractionated lignin has been performed. This was carried out in order to explain the colour-reducing effect of slaker-lime on the effluent. Turbidimetric, Atomic Adsorption and Calcium Ion Electrode techniques were used to study the various calcium species, as a function of pH. Following this, zeta potential experiments were performed with calcium hydroxide and slaker-lime; as a function of pH and lignin concentration.

The results obtained from this study showed the necessity for further work to be carried out on well-characterized lignin samples. Two lignin types; Kraft lignin, produced in Kraft pulping process and neutral sulphite semi-chemical (NSSC) ligno-sulphonates from the NSSC process, are being experimented with. Both lignin types have been purified. The Kraft lignin has been fractionated using gel permeation chromatography.

Lignin titrations have been carried out, and are expected to provide information on the presence or absence of conformational changes in solution. Ultimately, molecular weights will be determined for the fractionated lignin samples which will then be used in further titration and adsorption studies.

Background Salt Dependence on the Adsorption of Cadmium(II) at the Colloid/Water interface

Ian Harding (Melbourne)

A current theory explaining the phenomenon of enhanced adsorption at certain pHs of hydrolyzable metal ions is that resulting from the James - Healy approach. This is a thermodynamic approach in which the free energy of adsorption is divided into three parts: coulombic, solvation and chemical.

$$\text{i.e.} \quad \Delta G_{\text{ads}, i} = \Delta G_{\text{coul}, i} + \Delta G_{\text{solv}, i} + \Delta G_{\text{chem}, i}$$

The chemical term is generally considered to incorporate all specific interaction between the adsorbing species and the surface and is independent of the solution media, i.e., it should not be affected by inert electrolyte concentration.

Low dielectric solids such as SiO_2 , Al_2O_3 , FeOOH etc., are said to exhibit 'solvation controlled' adsorption. This term provides a strong barrier to adsorption for the species Cd^{2+} (aq). Adsorption does not occur unless the lower charged species, $\text{Cd}(\text{OH})^+$ (aq) forms. The pH dependence of such processes is relatively unaffected by inert electrolyte concentration. This was reflected in the Cd(II) adsorption process at such surfaces by a lack of background salt dependence.

High dielectric solids, such as TiO_2 , are said to exhibit 'coulombic' controlled adsorption. The solvation term is negligible with such solids, hence adsorption may occur as soon as the zeta-potential becomes favourable. The extent of adsorption is dependent on the magnitude of the surface potential. Inert electrolyte affects this by reducing the zeta-potential magnitude at any given pH. This is reflected in the adsorption process by a dependence on salt concentration. Adsorption was shifted to higher pH's when the salt concentration was increased.

Problems occurred when a polystyrene, amphoteric latex was used as the substrate. Cd(II) was shown to exhibit a salt dependence on its pH-dependent adsorption, similar to TiO_2 . However, polystyrene latices have low dielectric constants and might be expected to behave similarly to SiO_2 . The James-Healy was thus found to be inadequate, in its present form, to qualitatively describe the adsorption of Cd(II) at the polystyrene latex/water interface.

Statistical Mechanics of Polar Liquids

Glen Walker (ANU)

While many people are familiar with the physics of solids and gases, very few know much about liquids. The talk explained a few of the underlying principles of liquid state physics. Moreover, the equations are extended from spherically symmetric potentials to more realistic ones. A particular interest was taken in polar fluids, especially water.

Adsorption of Cu(II) and Co(II) on Hydrrous Iron(III) Oxide

John McLelland (Bendigo CAE)

When Co(II) and Cu(II) are adsorbed onto hydrrous iron(III) oxide it is found that for an initially 10^{-4} M cation solution 50 % of the Co(II) and Cu(II) solution will adsorb at 8.5 and 5.6 respectively. Upon addition of Co(II) and Cu(II) simultaneously to the hydrrous oxide suspension it is found that the pH at which 50 % of the Cu(II) adsorbed is unaffected whereas the 50 %

adsorption of Co(II) increases from 8.5 to 9.4. Since 90 % of the Cu(II) is adsorbed before Co(II) adsorption begins and no Cu(II) is found at higher pH values Cu(II) adsorption is unaffected by the presence of Co(II). However, when Cu(II) is adsorbed it occupies the most desirable adsorption sites thus leaving very few sites for the Co(II) to adsorb onto. Therefore the higher the concentration of Cu(II) the larger the shift in 50 % adsorption of the Co(II). The maximum shift caused by the 5×10^{-4} M Cu(II) as opposed to 10^{-3} M Cu(II) is explained through the occurrence of precipitation rather than adsorption.

The Adsorption of Nonionic Surfactants onto Hydrophilic and Hydrophobic Surfaces

Peter Scales (Melbourne)

The effects of a series of polydisperse nonyl phenol ethoxylates on the natural wettability of hydrophobic and hydrophilic surfaces have been studied. Adsorption density, contact angle, and liquid - vapour surface tension measurements were made. Model surfaces in the form of silica, butylated silica, and methylated silica were used.

Adsorption density studies show a two step mechanism of surfactant adsorption by a hydrophilic substrate with a dependence on adsorption of the length of the ethylene oxide (hydrophilic) moiety of the nonionic molecule. Adsorption by a hydrophobic substrate shows a one step adsorption mechanism with no apparent ethylene oxide chain length dependence.

Contact angle measurements show the wettability of all surfaces to be very similar at high surfactant concentrations. Results are consistent with the formation of an adsorbed monolayer of nonionic molecules with a molecular orientation of the ethylene oxide moiety towards the aqueous phase, independent of the natural wettability of the original surface.

The Depression of Arsenic Minerals in the Flotation of Broken Hill Lead Concentrates

Keith Quast (S.A.)

There are definite economic and health benefits to be obtained from reducing the levels of arsenic minerals in lead concentrates. This was achieved using a variety of arsenic depressants (e.g., lime, Aerodepressants 610 and 633, potassium cyanide and ferricyanide, ferrous sulphate and sodium hypochlorite) in the lead cleaner stage of laboratory flotation testing on a lead-zinc ore from Broken Hill. The most effective depression was obtained using potassium cyanide at pH 10, where arsenic recovery levels were reduced by 75 %.

Electrophoretic mobility studies were conducted on hand-selected samples of galena (PbS) and loellingite (FeAs₂), and some divergences in mobility behaviour could be correlated with changes in flotation behaviour.

Crystallization Studies of Waxy Crude Oils - The Role of Polymer Inhibitors

Russell Mills (Monash)

The phenomenon of wax separation from petroleum fluids has been a problem to users of petroleum products for a long time. Effective additives which improve the low temperature flow properties of middle distillates are a relatively recent development and whilst there is an appreciable amount of literature regarding the practical aspects of their use, little has been published about the way in which they act. A particularly potent inhibitor is the Ethylene-Vinyl Acetate copolymer.

Some results from previous work in this department is presented and a mechanism of crystal habit modification has been proposed. However, before a complete theory can be proposed it is necessary to investigate the structural properties of the inhibitor to decide whether the mechanism of crystal habit modification occurs by surface adsorption of the inhibitor or by co-crystallization.

In this project Ethylene-Vinyl Acetate copolymers will be synthesized using a high pressure, temperature controlled autoclave.

After purification carefully fractionated and characterized copolymers will be used in studies of the crystal structure, nucleation kinetics and adsorption/desorption kinetics of some highly purified n-paraffins to decide on the correct mechanism of crystal habit modification.