

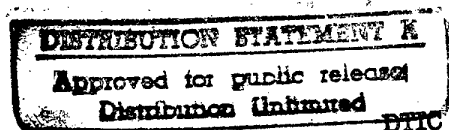
THIRD UK COLLOID AND SURFACE

SCIENCE STUDENT MEETING

The Lawns, University of Hull

16-19th July 1995

Organised by SCI Colloid and Surface Chemistry Group
in association with the RSC Colloid and Interface Science Group



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ABSTRACTS

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Dr. O. Elbayoumi,
Chief, Chemistry,
US Air Force,
EOARD,
223/231 Old Marylebone Road,
LONDON. NW1 5TH.



24th July, 1995.

Dear Dr. Elbayoumi,

3rd UK Colloid and Surface Science Student Meeting

Please find enclosed a short report of the above meeting held last week at the University of Hull, alongwith the Programme booklet, a delegate list and a copy of all abstracts. The meeting was a huge success, and I personally was staggered by the high quality of both the oral and poster presentations. I am sorry that you were in the end unable to attend the meeting - maybe next time at the University of Greenwich.

I am afraid it is now time to send an invoice to you for the remaining \$600 that your office pledged. I would appreciate it if the cheque is made payable to 'SCI' but forwarded to me as soon as possible. May I take this opportunity to thank the US Air Force on behalf of the Colloid and Surface Chemistry Group of the SCI for your generous donation.

INVOICE

To : EOARD, US Air Force
From : Dr. B.P. Binks, University of Hull
Amount : \$600
For : Sponsorship of the 3rd UK Colloid & Surface Science Student Meeting

With best wishes,

Dr. B.P. Binks

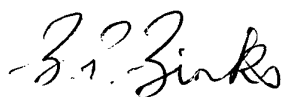
THIRD UK COLLOID AND SURFACE SCIENCE STUDENT MEETING

University of Hull, 16-19th July 1995

The above meeting took place recently and was a huge success. The meeting, the third of its kind, is organised by the Colloid and Surface Chemistry Group of the SCI and allows all postgraduates in the field of surface and colloid science to present their work orally or as posters to their own peers. In total, 110 research students, 14 academic supervisors and 13 industrial supervisors attended the conference held over two and a half days. Twenty five oral presentations were given mainly by final year students within session themes including Foams, Emulsions/Microemulsions, Surfactant/Polymer interactions, New experimental techniques, Surfactant monolayers and Phase behaviour studies. In addition, 88 posters were prepared and presented mainly by first and second year students. The UK students came from departments of Chemistry, Physics, Pharmacy, Chemical/Biochemical Engineering and Food Science; 4 students from abroad were also invited. The overall quality of all presentations was very high and it was clear that all student participants had worked hard and with great care prior to the meeting.

The meeting can only go ahead with generous donations from companies, institutes and government bodies. In all, 35 of these donated ~ £19,000 towards the running costs and the organiser is most grateful to them. The social programme included a quiz on Monday evening, an excursion to York on Tuesday afternoon and a Band after the conference dinner on Tuesday. Prizes were presented for the three best talks and the three best posters. It was clear by the end of the conference, and from feedback since, that all participants had thoroughly enjoyed both the scientific content as well as the other events laid on. There was a good integration of all students from the different departments, and there was an opportunity to discuss and liaise with the scientists from companies and the academic staff.

The 4th meeting is planned for 2 years time to be held at the University of Greenwich. This series of meetings has certainly gained momentum and I am certain that the next meeting will be as popular and as successful as this one has been.



Dr. B.P. Binks, Organiser

School of Chemistry, University of Hull

24/7/95

SCI



THIRD UK COLLOID AND SURFACE SCIENCE STUDENT MEETING

The Lawns, University of Hull

16-19 July 1995

Organised by the
SCI Colloid & Surface Chemistry Group
in association with the
RSC Colloid & Interface Science Group

PROGRAMME

SUNDAY 16 JULY

14.00 - Registration
18.00

19.00 Dinner

20.00 Poster Session I

MONDAY 17 JULY

08.00 Breakfast

08.40 Introduction
B P Binks, University of Hull

Chairperson: Dr R Aveyard, University of Hull

08.45 Stabilisation of protein adsorbed layers in foams and emulsions
by crosslinking
D K Sarker, Institute of Food Research, Norwich

09.10 Surfactant stabilised gas microcells
S Brockbank, University of Bristol

09.35 Colloidal gas aphrons (CGAs) as a potential technique for
protein recovery
P Jauregi, University of Reading

10.00 The attachment of hydrophobic particles onto rising air bubbles
within the context of antifoaming systems
P K Elks, University of Bristol

10.25 Coffee

Chairperson: Dr P F Luckham, Imperial College, London

10.45 NMR studies of transfer rates in emulsions
M R Powell, University of Nottingham

11.10 Creaming of oil in water emulsions
V J Pinfield, University of Leeds

- 11.35 Novel monodisperse 'silicone oil'/water emulsions
D O H Teare, University of Bristol
- 12.00 Microemulsion based gels for transdermal drug delivery
S Kantaria, King's College, London
- 12.30 Lunch
- Chairperson: Dr A M Howe, Kodak Ltd, Harrow*
- 14.00 Adsorption of polyelectrolytes and surfactants from solution and
their competitive behaviour
I M Harrison, North East Wales Institute
- 14.25 Adsorption studies on mixed silica, polymer, surfactant systems
S J Mears, University of Bristol
- 14.50 Hydrodynamic erosion of surface coatings
M J Pickles, Imperial College, London
- 15.15 Particle removal and deposition at three-phase contact lines
C M Croll, University College, London
- 15.40 Tea
- Chairperson: Dr T Cosgrove, University of Bristol*
- 16.00 Study of surface forces of an adsorbed PEO layer using a silica
particle probe SFM
G J C Braithwaite, Imperial College, London
- 16.25 Recent advances in the study of dissolution kinetics using the
scanning electrochemical microscope
J V Macpherson, University of Warwick
- 16.50 - 18.30 Poster Session II
- 19.30 Dinner following by evening lecture entitled "Reflections from a
Superficial Scientist" by Professor Brian A Pethica, Columbia
University, USA

21.30 Quiz in the bar led by P A Kingston, Hull

TUESDAY 18 JULY 1995

08.00 Breakfast

Chairperson: Dr J H Clint, University of Hull

08.45 Sum-frequency spectroscopy of tri-chain surfactants and
dodecanol coadsorbed at a hydrophobic surface
M S Johal, University of Cambridge

09.10 A quartz crystal microbalance study of the rate of diffusion of
entrained water through model LB films
M R Lovell, University of Bath

09.35 Sonochemistry and colloids
R Hobson, University of Melbourne

10.00 Small-angle neutron scattering studies of surface adsorbed
dispersing agents on pigment particles
J M Gladman, University of Salford

10.25 Coffee

10.45 Poster Session III

12.30 Lunch

14.00 Depart for York

18.00 Commence return from York

20.00 Conference Dinner
Speech by Dr A Hayes CBE, President of SCI
Presentation of 1995 Beilby Medal and Prize to Dr L F Gladden,
Department of Chemical Engineering, University of Cambridge
Presentation of poster prizes

22.00 Band

WEDNESDAY 19 JULY

08.00 Breakfast

Chairperson: Dr M J Hey, University of Nottingham

08.45 The interaction of oils with surfactant monolayers
J R MacNab, University of Hull

09.10 Thermodynamic relation of an insoluble monolayer at the oil/water
interface and at the air/water interface in contact with oil
M Thoma, University of Mainz

09.35 Interfacial studies of a binary surfactant mixture
J Hines, University of Oxford

10.00 Experimental study of the breakage and melting of a two-dimensional
crystal
L Pauchard, École Normale Supérieure, Paris

10.25 Coffee

Chairperson: Dr M J Lawrence, King's College, London

10.45 An inverse micellar cubic phase formed by phosphatidylcholine/fatty
acid and phosphatidylcholine/fatty alcohol mixtures
Z Huang, Imperial College, London

11.10 Highly ordered aggregates in dilute dye-water systems
D L Mateer, University of Salford

11.35 Investigations of liquid crystalline phases using microscopy,
differential scanning calorimetry and rheological techniques
G T Dimitrova, Imperial College, London

12.00 Dynamic and equilibrium properties of new sugar surfactants
P Rogueda, University of Bristol

Presentation of prizes for orals

12.30 Lunch and close

ORGANISED BY

Dr B P Binks
Surfactant Science Group, School of Chemistry
University of Hull, Hull HU6 7RX

ABSTRACT COMMITTEE

Dr B P Binks, University of Hull
Dr T Cosgrove, University of Bristol
Dr A M Howe, Kodak Ltd, Harrow
Dr M J Lawrence, King's College, London
Dr S J Lenon, ICI Paints, Slough
Dr P F Luckham, Imperial College, London

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16-19 July 1995

DELEGATE LIST

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Chemistry Group in association with the
RSC Colloid & Interface Science Group

3rd UK COLLOID & SURFACE SCIENCE STUDENT MEETING
LIST OF DELEGATES
16 - 19 JULY 1995

Ahmad Mr J J	Kings College London London UK
Akram Miss G	University of Nottingham Nottingham UK
Al-Assaf Mr S	The North East Wales Institute Deeside UK
Anderson Miss R L	Heriot Watt University Galashiels UK
Anderson Mr S J	ICI Surfactants Middlesbrough UK
Andrews Mr C S	The University of Brighton Brighton UK
Aveyard Dr R	University of Hull Hull UK
Barlow Dr R J	ZENECA Pharmaceuticals Macclesfield UK
Bean Mr K H	University of Bristol Bristol UK
Biffen Miss A M	The North East Wales Institute Deeside UK
Binks Dr B P	University of Hull Hull UK
Braithwaite Mr G J C	Imperial College of Science Technology & Medicine London UK
Brant Miss J A	The University of Brighton Brighton UK
Briggs Mr A M	Cambridge University Cambridge UK
Brockbank Miss S	University of Bristol Bristol UK
Butterworth Dr M	University of Sussex Brighton UK
Calpin-Davies Miss S R	University of Bristol Bristol UK
Carlile Miss K	University of East Anglia Norwich UK
Cho Mr W G	University of Hull Hull UK

Clegg Mr F C	Sheffield Hallam University Sheffield UK
Clint Dr J H	University of Hull Hull UK
Cooke Miss D J	Oxford University Oxford UK
Corradi Mr R	University of Sussex Brighton UK
Cosgrove Dr T	University of Bristol Bristol UK
Cox Mr A R	University of Bristol Bristol UK
Cox Miss J K	University of Bristol Bristol UK
Croll Ms C M	University College London London UK
Crooks Miss E R	University of Bristol Bristol UK
Darwent Dr J R	Unilever Research Wirral UK
Dimitrova Miss G T	ZENECA Agrochemicals Bracknell UK
Dong Miss J F	University of Bristol Bristol UK
Douglas Mrs A	University of Hull Hull UK
Elks Miss P K	University of Bristol Bristol UK
Evans Mr R M	Sheffield Hallam University Sheffield UK
Ezomo Mr F A S	Imperial College of Science Technology & Medicine London UK
Fairbrother Mr R	University College London London UK
Fessey Mr R E	University of Liverpool Liverpool UK
Finnigan Miss M E	University of Bath Bath UK
Fitzpatrick Mr P	The North East Wales Institute Deeside UK

Fletcher Miss A L	Cambridge University Cambridge UK
Froggatt Miss E S	University of Bristol Bristol UK
Ghezzi Mr F G	Queen's University of Belfast Belfast UK
Gladman Miss J M	University of Salford Salford UK
Golding Mr M D	University of Leeds Leeds UK
Graf Mr K	Institute for Physical Chemistry Mainz Germany
Gray Mr J	University of Salford Salford UK
Green Mr N D	University of Bristol Bristol UK
Gregory Mr P J	University of Exeter Redruth UK
Gutron Miss C	Université de Montpellier II Montpellier France
Hagan Miss S A	University of Nottingham Nottingham UK
Harding Mr R	University of Leeds Leeds UK
Harrison Mr I M	The North East Wales Institute Deeside UK
Harrison Mr M B J	Queen's University of Belfast Belfast UK
Hartley Dr P	University of Melbourne Parkville Australia
Hawkins Mr J	Albright & Wilson Whitehaven UK
Hetherington Miss K j	University of Bristol Bristol UK
Hey Dr M J	University of Nottingham Nottingham UK
Hines Mr J D	Oxford University Oxford UK
Hobson Miss R A	University of Melbourne Parkville Australia

Hong Mr S T	University of Leeds Leeds UK
Hou Mr R	University of Exeter Redruth UK
Howe Dr A M	Kodak Ltd Harrow UK
Huang Mr Z	Imperial College of Science Technology & Medicine London UK
Hussain Mr A	Imperial College of Science Technology & Medicine London UK
Islam Miss A M	University of Greenwich London UK
Jauregi Miss P	University of Reading Reading UK
Jefferson Mr B	Loughborough University of Technology Loughborough UK
Johal Mr M S	Cambridge University Cambridge UK
Johnson Mr E G	Queen's University of Belfast Belfast UK
Kantaria Mrs S	Kings College London London UK
Khan Mr A U	Imperial College of Science Technology & Medicine London UK
Kippax Mr P G	University of Nottingham Nottingham UK
Kneebone Dr G R	AgrEvo UK Ltd Cambridge UK
Kutzner Miss H B	Imperial College of Science Technology & Medicine London UK
Lascelles Mr S F	University of Sussex Brighton UK
Lawrence Dr C J	Imperial College of Science & Technology London UK
Lawrence Dr M J	King's College University of London London UK
Lenon Dr S J	ICI Paints Slough UK
Lin Mr W	University of Nottingham Nottingham UK

Locke Mr C J	Shell Research Ltd Chester UK
Lovell Mr M R	University of Bath Bath UK
Loxley Mr A L	University of Bristol Bristol UK
Ma Mr G K F	Kings College London London UK
MacNab Mr J R	University of Hull Hull UK
Macpherson Miss J V	University of Warwick Coventry UK
Maitland Dr G C	Schlumberger Cambridge Research Cambridge UK
Manimaaran Mr S	Imperial College of Science Technology & Medicine London UK
Mark Mr A	Coulter Electronics Ltd Luton UK
Marshall Miss S J	University of Wales College of Cardiff Cardiff UK
Mateer Mrs D L	University of Salford Salford UK
McFayden Mr P	Brookhaven Instruments Ltd Stock Wood UK
Mears Miss S J	University of Bristol Bristol UK
Misran Mr M	University of East Anglia Norwich UK
Moore Mr C R	University of Bath Bath UK
Neal Mr J C	University of Nottingham Nottingham UK
Patel Mr R	Kings College London London UK
Pauchard Mr L	Ecole Normale Supérieure Paris France
Pawlowsky Miss K M D	University of Leeds Leeds UK
Pickles Mr M J	Imperial College of Science Technology & Medicine London UK

Pinfield Miss V J	University of Leeds Leeds UK
Powell Mr M R	University of Nottingham Nottingham UK
Price Miss A L	University of East Anglia Norwich UK
Rana Mr F	University of Salford Salford UK
Redhead Miss H M	University of Nottingham Nottingham UK
Richardson Mr C J	Kings College London London UK
Rodham Dr D K	ZENECA Agrochemicals Bracknell UK
Rogueda Mr P	University of Bristol Bristol UK
Rossi Miss S	Imperial College of Science Technology & Medicine London UK
Rough Miss S L	Imperial College of Science Technology & Medicine London UK
Sammon Dr C	Sheffield Hallam University Sheffield UK
Sargeant Mr D L	University of East Anglia Norwich UK
Sarker Mr D K	Institute of Food Research Norwich UK
Satra Mrs C H	Kings College London London UK
Shewring Mr N I E	Sheffield Hallam University Sheffield UK
Simmons Mr M R	University of Sussex Brighton UK
Simons Dr S J R	University College London London UK
Smith Miss K	Imperial College of Science Technology & Medicine London UK
Snowden Dr M J	University of Greenwich London UK
Sostaric Mr J Z	University of Melbourne Parkville Australia

Stebbing Mr S R	University of Bristol Bristol UK
Teare Mr D O H	University of Bristol Bristol UK
Thoma Mr M	Institute for Physical Chemistry Mainz Germany
Thompson Mr R L	University of Hull Hull UK
Thoraval Miss C F	University of Reading Reading UK
Vamvakaki Mr M S	University of Sussex Brighton UK
Walsh Mr J M	Unilever Research Wirral UK
Ward-Smith Dr S	Malvern Instruments Malvern UK
Warisnoicharoen Miss W	Kings College London London UK
Weatherhead Mr I	University of Bristol Bristol UK
Webster Dr J R P	Rutherford Appleton Laboratory Didcot UK
Wegener Mr M R	University of Bristol Bristol UK
West Mr W	Imperial College of Science Technology & Medicine London UK
Wickham Mr M S J	Institute of Food Research Norwich UK
Wicks Ms A C	University of Hull Hull UK
Williams Miss L	UMIST Manchester UK
Willmer Miss S A	Loughborough University of Technology Loughborough UK
Wright Mr N G	University of Bristol Bristol UK
Yan Mrs H	University of Nottingham Nottingham UK
Zhu Mr S	Imperial College of Science Technology & Medicine London UK

We wish to thank the following for their financial sponsorship of this meeting :

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This book of abstracts is arranged in the following manner :

Oral communications are given the letter 'O' followed by a number. The order is the order given in the Programme.

Poster communications are given the letter 'P' followed by a number. The order is the alphabetical order of the presenting author.

B.P. Binks

1/6/95

ORALS

STABILISATION OF PROTEIN ADSORBED LAYERS IN FOAMS AND EMULSIONS BY CROSSLINKING

Dipak K. Sarker, Peter J. Wilde and David C. Clark

Institute of Food Research, Norwich Research Park, Colney Lane, Norwich, NR4 7UA,
UK.

Foams and emulsions which are stabilised by proteins e.g. beer foams and meringues remain stable in the absence of small molecular weight surface active components (lipids, emulsifiers and surfactants). In the presence of surfactants the stabilising visco-elastic layer of protein surrounding each particle is compromised due to competitive adsorption of the surfactant. One strategy to overcome these partially stable dispersions is to unite the 'mobilised' regions of protein adsorbed at the air-water or oil-water interface and produce a more continuous layer of adsorbed protein.

A model foam composed of precise amounts of surface active protein, β -lactoglobulin (β -lg) and an emulsifier, Tween 20, to mimic the destabilisation of food foams and emulsions was used as a test sample to assess the effectiveness of various potential crosslinking agents.

Addition of micromolar concentrations of the polyphenol, (+)catechin and a trivalent cation, Al^{3+} were found to increase the foam formation and foam stability (reduced liquid drainage from the foam). Behaviour of the model foams has been related to the (+)catechin and trivalent cation mediated crosslinking of protein adsorbed at the interface in thin liquid films (foam lamellae).

SURFACTANT STABILISED GAS MICROCELLS

R.D. Bee^a, J. Bringham^a, S. Brockbank^b, D. Ferdinando^a and R.H. Ottewill^b

a Unilever Research Laboratory, Colworth House, Bedfordshire, MK44 1LQ

b School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

Stable foams have been produced by the aeration of 2% w/w sucrose mono-, di- and tri- stearate in a medium of 75% w/w maltodextrin syrup, Sweetose. The constituents were heated to 80°C, and aerated for two hours at room temperature. The aerated and non-aerated mixtures were examined by microscopy and differential scanning calorimetry. SEM was used to examine the cell size distribution as a function of aeration time. Viewing the aerated mixture by TEM revealed 0.2-20µm gas microcells, possessing a structured interface comprising hexagonal and pentagonal protruding domes of 50-100nm diameter¹. Confocal scanning laser microscopy revealed air bubbles encased by the non-aerated mixture with a broad birefringent interface and a distinctive surface texture. Detail at the surface of the gas microcells was not seen. DSC indicated an endothermic transition at 48°C in the non-aerated mixture which was not initially present in the aerated mixture but which appeared on secondary heating. It is proposed that the sucrose ester surfactant forms layers of liquid crystal at the interface which limits disproportionation, hinders drainage and hence stabilises the gas microcells.

1. "Gas cells in a liquid medium", R.D. Bee, Unilever P.L.C., PCT Int. Appl.

WO92 21, 225

Dr R.D. Bee
Unilever Research Laboratory
Colworth House
Sharnbrook
Bedfordshire.
MK44 1LQ

COLLOIDAL GAS APHRONS (CGAs) AS A POTENTIAL TECHNIQUE FOR PROTEIN RECOVERY

Paula JAUREGI and Julie VARLEY

Biotechnology and Biochemical engineering group, Department of Food Science and Technology, University of Reading, Reading RG6 2AP

Colloidal gas aphones are micron sized gas bubbles coated by a thin surfactant film, which are created by intense stirring of a surfactant solution. Their size (10-100 μm) and structure confers to them colloidal behaviour therefore electrostatic, hydrophobic and surface forces will be the main forces governing this type of system.

Some properties deriving from their particular structure, such as high interfacial area due to their small size, high stability due to the surfactant shell surrounding the gas bubble and the possibility of different mechanisms (hydrophobic and electrostatic interactions) for protein adsorption, indicate that these dispersions may have potential when used for protein recovery.

The present study mainly focuses on the characterisation of CGAs. Results from statistically designed experiments show the effect of different factors including: power consumption and bubble size distribution, on the stability of CGAs. At the same time, protein-surfactant interactions were studied in order to optimise protein recovery for an AOT-lysozyme system.

Basque Government. Eusko Jauriaritza-Gobierno Vasco, Duque de Wellington 2, 01010 Vitoria-Gasteiz, Spain

THE ATTACHMENT OF HYDROPHOBIC PARTICLES ONTO RISING AIR BUBBLES WITHIN THE CONTEXT OF ANTIFOAMING SYSTEMS.

P.K. Elks¹, B. Vincent¹ and P.R. Garrett².

¹Department of Physical Chemistry, School of Chemistry, University of Bristol. Cantock's Close. Bristol BS8 ITS.

²Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral. L63 3JW.

The model of a single spherical air bubble rising through a dilute suspension of hydrophobed glass microspheres has been used to study the effect of aqueous phase composition on particle collection efficiency, as a function of bubble diameter.

In the past this technique has been used to study the mechanism by which particle attachment occurs in flotation systems for various particle geometries. In this paper we continue with this approach but within the context of antifoaming systems. We show that omissions in the analysis exist in the early work with regard to the random statistical fluctuations of collected particle numbers and show that the resulting spread in the particle collection efficiency data is characterised by a Poisson distribution for a fixed bubble size.

Here we present particle collection efficiency data for fixed bubble sizes and a range of systems within a sliding regime of particle attachment.

Unilever Research, Port Sunlight Laboratory. Quarry Road East, Bebington, Wirral L63 3JW.

NMR STUDIES OF TRANSFER RATES IN EMULSIONS

Matthew R Powell, Michael J Hey and Derrick C Dobson*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD
*ICI Surfactants, PO Box 90, Wilton Centre, Middlesbrough,
Cleveland TS90 8JE

The permeation of liquid-liquid interfaces by solutes is usually studied under conditions of net material transfer when the interfacial resistance may be dominated by a stagnant boundary layer. A method based on the analysis of nmr lineshapes has been developed which gives the rate of solute transfer between the oil and water phases of an emulsion. When combined with droplet size data, the nmr measurements allow a parameter to be calculated which is characteristic of the barrier properties of the interface.

Data will be presented for the transfer rates of 1,4 dioxan and tetrahydrofuran across o-xylene/water interfaces stabilised by mixtures of commercial, non-ionic surfactants. The results which enable the optimum formulations for stability to be found will be discussed in the context of the HLB (hydrophile-lipophile balance) system.

ICI Surfactants, PO Box 90, Wilton Centre, Middlesbrough, Cleveland TS90 8JE

CREAMING OF OIL IN WATER EMULSIONS

Eric Dickinson, Valerie J Pinfield and Malcolm J W Povey

Procter Department of Food Science, University of Leeds

Creaming in emulsions is a significant destabilisation process in food systems, and in other applications of emulsions, for example in the pharmaceutical industry. Studies of creaming may lead to greater understanding of the effects of stabilisers and other additives in such systems.

Time-dependent measurements of ultrasound velocity are used to obtain concentration profiles in emulsions during creaming, and the relationship between velocity and oil concentration is considered. Numerical simulations are presented of creaming in an idealised emulsion, together with calculation of the corresponding ultrasound velocity profiles. The simulations provide information on the correct interpretation of ultrasound velocity measurements. Comparison of the numerically generated concentration profiles with experimental results show evidence of particle interactions e.g. flocculation in the experimental systems.

The presentation aims to show how the use of ultrasound and numerical simulation can aid our understanding of the behaviour of emulsions undergoing creaming.

NOVEL MONODISPERSE "SILICONE OIL" / WATER EMULSIONS

Declan O.H. Teare, Timothy M. Obey and Brian Vincent

School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

The preparation of liquid "latex" particles, namely monodisperse droplets of "silicone oil" in water, in the absence of added surfactants, has been carried out via the base-catalysed hydrolysis and polymerisation of dimethyldiethoxysilane in water or water / ethanol mixtures. This method is analogous to the nucleation and growth of colloidal silica particles. The physical properties of the emulsions produced have been studied using dynamic light scattering and electrophoresis. Analysis of the "silicone oil" phase using ^1H and ^{29}Si NMR has shown that, depending on the amount of ethanol in the reaction mixture, the oil phase consists of a mixture of cyclic and linear (oligomeric) poly(dimethylsiloxane). Stability of the emulsions is provided by a charge originating from ionisation of terminal silanol groups on the linear chains. Results are presented on the effects of solubilising hydrocarbons in the emulsions and of adding the *tri*-functional monomer, in addition to the *di*-functional one.

Bristol University Postgraduate Scholarship

University of Bristol, Senate House, Tyndall Avenue, Bristol BS8 1TH

MICROEMULSION BASED GELS FOR TRANSDERMAL DRUG DELIVERY

S. Kantaria and M.J. Lawrence

Department of Pharmacy, King's College London, Manresa Rd., London

Water-in-oil microemulsions have been shown to form gels (known as microemulsion based gels (MBG)) upon the addition of gelatin¹. We have investigated the use of these novel oil-based conducting gel systems for the transdermal delivery of water soluble drugs using iontophoresis. Iontophoresis is the application of an electric current to a drug on the surface of the skin in order to deliver that drug into the skin. To date however MBG have only been formed using pharmaceutically unacceptable surfactants and oils, such as aerosol OT and heptane. In order to circumvent this limitation we have examined the formation of MBG in a wide range of pharmaceutically acceptable surfactants and oils. In particular, the oils, isopropyl myristate and isopropyl palmitate and the nonionic surfactants, the n-alkyl polyoxyethylene ethers and the n-acyl polyoxyethylene sorbitan esters have been extensively studied.

It has been found that carbon chain length of the oil, the number of polyoxyethylene groups present within the surfactant were important in determining the area of existence of the resulting water-in-oil microemulsions. Interestingly while it was possible to produce water-in-oil microemulsions with the majority of surfactants studied, it was not found possible to gel them unless a small amount of aerosol OT was present in the microemulsion. From a knowledge of head group hydration it was calculated that, in microemulsions containing only a polyoxyethylene surfactant, there was not a large enough water pool to allow hydration of the added gelatin, a pre-requisite for gel formation. Since these MBG are intended as devices for the iontophoretic delivery of drug the above studies were repeated in the presence of a model water soluble drug, sodium salicylate. It was found that the presence of sodium salicylate appreciably influenced MBG formation, reducing the number of systems that could produce MBG. It was established that concentrations of sodium salicylate no greater than 10%w/v of the aqueous pool could be incorporated into an MBG. The results obtained are discussed in relation to the application of MBG as vehicles for iontophoretic drug delivery.

1. G. Haering and P.L. Luisi, *J. Phys. Chem.*, 1986, **90**, 5892.

ADSORPTION OF POLYELECTROLYTES AND SURFACTANTS FROM SOLUTION AND THEIR COMPETITIVE BEHAVIOUR, I. M. Harrison and I. D. Robb, Centre of Expertise for Water Soluble Polymers, MRIC, NEWI, Deeside, Clwyd, CH4 4BR

Competitive adsorption between polymer-polymer and polymer-surfactant systems (known to have the same adsorbing group) onto solids would expect to be determined by kinetic and thermodynamic equilibria. The adsorption of a cationic polyelectrolyte (polymer JR) and cationic surfactant (CTAB) onto silica has been investigated. Competitive adsorption between polymers of varying molecular weight resulted in a long term preferential adsorption of the lower molecular weight material, as may be predicted from the theories of polyelectrolyte adsorption. This is a result of kinetic stability rather than thermodynamic stability. Similarly, competitive adsorption between polymer JR and CTAB led to preferential adsorption of the surfactant with almost a total exclusion of the polymer indicating again kinetic rather than thermodynamic stability. Surprisingly, in the presence of CTAB, the lower molecular weight polymer adsorbed to a smaller extent than the higher molecular weight material, in contrast to that occurring in the absence of surfactant. Preadsorption of polymer JR onto the silica surface followed by the addition of surfactant caused desorption of the polymer to a small extent showing the thermodynamically stable end result. Coating the silica surface with various levels of CTAB, even to levels less than that required for charge neutralisation, caused almost total exclusion of the polymer from the surface. These observations, and their subsequent effect on colloid stability, are interpreted in terms of relative thermodynamic and kinetic equilibria.

**ADSORPTION STUDIES ON MIXED SILICA, POLYMER,
SURFACTANT SYSTEMS.**

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Photon correlation spectroscopy, neutron scattering and nuclear magnetic resonance spectroscopy measurements have been performed on aqueous silica dispersions containing physisorbed poly(ethylene oxide) in the presence of the surfactant sodium dodecyl sulphate. From these measurements, it appeared that near complete desorption of the polymer occurred around the critical micelle concentration of the pure surfactant. However, at very high surfactant concentrations, the apparent hydrodynamic thickness returned to its initial value in the absence of surfactant. The results are discussed in terms of the specific interactions between the polymer and the surfactant.

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HYDRODYNAMIC EROSION OF SURFACE COATINGS

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In many industrial processes, complex and multi-component surface fouling layers build up at the walls of process equipment, which may reduce the efficiency of material transport or heat transfer. These layers must therefore be removed and this is often achieved by using fluid to erode the layer hydrodynamically. This project aims to investigate the processes involved in the erosion of surface coatings and contaminants under the action of hydrodynamic flows. A radial flow cell and a high-pressure liquid jet apparatus have been used to erode a variety of model coatings and the erosion rates quantified using a laser profilometry technique. The mechanical and interfacial properties of these model coatings have also been measured, by using the micro-indentation and blister test techniques to obtain values of hardness, Young's modulus and interface fracture energy. Comparisons have been made between the observed erosion characteristics of the coatings and their mechanical and interfacial properties.

Industrial Sponsors: [†]Unilever Research, Port Sunlight Laboratory,
Quarry Road East, Bebington, Wirral, Merseyside. L63 3JW

PARTICLE REMOVAL AND DEPOSITION AT THREE-PHASE CONTACT LINES

by C.M.CROLL and J.GREGORY

University College London

Deposition and removal of particles in the region of the three-phase contact line (solid/liquid/gas) could be significant in a wide variety of systems such as trickling filters, heat exchangers, air-scouring in granular filters, transport of pollutants in soils and aquifers and hard surface cleaning.

This investigation compared laminar flow and laminar flow with bubble injection through a tube. The removal rates of pre-deposited particles were studied (weakly and firmly adhered). Results showed that particles were more readily removed by the passage of a bubble.

Further work using the same conditions as above have shown that the bubble rear removes most of the pre-deposited particles and at lower flow rates more particles are removed by the passage of an air bubble.

Dr.M.Garvey
Unilever Research Portsunlight

STUDY OF SURFACE FORCES OF AN ADSORBED PEO LAYER USING A SILICA PARTICLE PROBE SFM. G. J. C. Braithwaite*, P. F. Luckham*,
*Department of Chemical Engineering, Imperial College, London SW7 2BY, UK, A. M. Howe+, +Kodak Ltd, Headstone Drive, Harrow HA1 4TY, UK.

After the advent of the Scanning Tunnelling Microscope and laterally the Scanning Force Microscope (SFM) in 1986 there has been a huge increase in interest in the study of nanometer scale properties. However up until recently this interest has only produced studies of the topography of surfaces. This has under-used the potential of the technique, in the area of surface forces and more particularly in the determination of colloidal properties.

In this presentation the construction of a custom built force sensor using the optical lever techniques developed for commercial SFM's will be described. This device has been used to probe the interactions between silica particles and a mica surface as a function of electrolyte concentration. The interactions of the same surfaces, where both surfaces bear adsorbed polyethyleneoxide have also been studied. The results are compared to theoretical predictions based on electrical double layer theory for the interactions between the charged surfaces of silica and mica, and scaling theory for the interactions between the adsorbed polymers. In the latter case the results are also compared and contrasted to those obtained using the mica surface force apparatus.

Kodak Ltd, Headstone Drive, Harrow HA1 4TY, UK

RECENT ADVANCES IN THE STUDY OF DISSOLUTION KINETICS USING THE SCANNING ELECTROCHEMICAL MICROSCOPE

Julie V. Macpherson and P. R. Unwin, Dept. of Chemistry, University of Warwick,
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The Scanning Electrochemical Microscope (SECM) is a scanned probe device in which the Faradaic current response of an ultramicroelectrode (UME), positioned or scanned in close proximity to a sample interface, is used to probe interfacial reactivity or topography at the micrometer level. For dissolution studies, the UME is used to initiate and monitor the reaction of interest through the electrolysis of a suitable solution species. The sensitivity of the corresponding tip current response to the reactivity of the interface, coupled with the fact that this can be addressed theoretically, makes SECM a powerful technique for quantitative investigations of dissolution phenomena. In this talk it will be shown that SECM allows answers to be provided to the following questions, for a wide range of crystal solubilities:

- (i) How are microscopic surface structure, surface charge and reactivity interrelated?
- (ii) What is the role of the "inert" electrolyte?
- (iii) How do rates and mechanisms depend on concentrations at the interface?

SUM-FREQUENCY SPECTROSCOPY OF TRI-CHAIN SURFACTANTS AND DODECANOL COADSORBED AT A HYDROPHOBIC SURFACE

Malkiat S. Johal, Robert N. Ward, Paul B. Davies*, Adam M. Briggs, Eric W. Usadi.

Department of Chemistry, University of Cambridge.

The applications of surfactants are diverse. Their ability to solubilise in water a variety of otherwise insoluble materials is critical in detergency as well as in the stabilisation of both macroemulsions and microemulsions. Despite their undoubted importance, the behaviour of surfactants at interfaces is poorly understood at the molecular level due to a lack of appropriate surface-analytical probes. Sum-frequency spectroscopy (SFS) is an excellent candidate for such *in-situ* studies. The capabilities of the technique are exemplified by our studies of the coadsorption of dodecanol and tri-chain surfactants from aqueous solution onto a flat hydrophobic surface. These mixtures were studied above and below the critical micelle concentration (cmc) of the tri-chain.

Below the cmc, coadsorption of the two surfactants occurs. At low concentrations of the tri-chain, the dodecanol displaces most of the tri-chain from the surface. At tri-chain concentrations just below the cmc, dodecanol simply adsorbs in the gaps around the tri-chain molecules, neither displacing the tri-chain molecules nor increasing their low conformational and orientational order. The corresponding order of the dodecanol is high in these films, just as it is in the absence of tri-chain. The tri-chain molecules are pictured as individuals or small clusters amid a "sea" of dodecanol.

Above the cmc and in the absence of salt, only the tri-chain adsorbs from the mixed solutions. However, if 0.1 M NaCl is added to these solutions, both tri-chain and dodecanol adsorb. The surfactant aggregates in salt-free solution are apparently able to completely solubilise dodecanol and so prevent it adsorbing to the hydrophobic surface. It is possible that salt reduces the curvature of the aggregates and effectively squeezes the dodecanol out into solution, from where it is able to coadsorb to the surface. This exciting result has initiated investigations into the adsorption from salt-stabilised microemulsions involving tri-chains.

Dr. Andrew Clarke. Kodak Ltd., Headstone Drive, Harrow. Middlesex. HA1 4TY.

A QUARTZ CRYSTAL MICROBALANCE STUDY OF THE RATE OF
DIFFUSION OF ENTRAINED WATER THROUGH MODEL LB FILMS.

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An integrated form of Fick's 1st law has been used to model the characteristic drying curves of behenic acid ($\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$) monolayers, and its metal derivatives (Cd, Mn, Ca) deposited vertically on a quartz crystal microbalance using the Langmuir-Blodgett (LB) technique. The model combines the first order kinetics of diffusion through fatty acid regions with that through salt regions to successfully describe the drying purely in terms of the transport of water molecules outwards perpendicular to the layers of the film. There is no lateral migration of water molecules in the plane of the layers towards pin-holes in the LB film, or its edges, where the water would evaporate at a much faster rate. Preliminary results show that diffusion through fatty acid regions is slower than through salt regions, the diffusion coefficient for the acid films being, in general, an order of magnitude smaller than that for the salt layers.

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SONOCHEMISTRY AND COLLOIDS

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The absorption of high intensity ultrasound by water is known to produce H and OH radicals in solution. This is due to a phenomenon known as acoustic cavitation; the formation, growth and collapse of small bubbles in the sonicated solution. These primary radicals can be scavenged by other chemical species in solution to produce secondary radicals. Subsequently further chemical reactions may occur. The reduction of the water soluble metal ion, AuCl_4^- , sonicated in the presence of alcohols and surfactants, generating colloidal gold particles has been studied. It has been found that by altering the type and quantity of the surfactant in solution the yield of the gold particles also changes. The efficiency of gold formation is dependent on the air/water surface activity of the surfactant used, implying that the scavenging of the primary radicals occurs at the cavitation bubble liquid interface.

SMALL-ANGLE NEUTRON SCATTERING STUDIES OF SURFACE ADSORBED DISPERSING AGENTS ON PIGMENT PARTICLES

J.M.Gladman, T.L.Crowley, Dept. of Chemistry, University of Salford, Salford

J.D.Schofield, Zeneca Specialities, Blackley, Manchester

Small-angle neutron scattering is used to investigate the structure of surface adsorbed dispersing agents, on copper phthalocyanine pigment particles, in aqueous dispersion. The aim is to correlate structural parameters of the adsorbed layer with the effectiveness of the dispersing agent and then to relate this to the structure of the surfactant and to the level surfactant loading.

By using contrast variation, achieved by using H_2O/D_2O mixtures of different composition, it is possible to determine several important structural parameters of the surfactant layer e.g. the adsorbed amount and the adsorbed layer thickness. These parameters were measured for a range of surfactants, as a function of surfactant loading.

The results are discussed in relation to experimental and molecular modelling studies of surfactant/pigment binding.

Dr. J.D.Schofield, Zeneca Specialities, Blackley, Manchester

THE INTERACTION OF OILS WITH SURFACTANT MONOLAYERS

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A wide range of water-insoluble oils can be "solubilised" in aqueous solution with the aid of suitable surfactants. In this process the oil material is dissolved within the apolar core of surfactant micellar aggregates but the interaction between the oil and surfactant is currently poorly understood. Since solubilisation is important in many technological processes, there is a need to understand the interactions of oils with surfactant monolayers.

One means of studying oil/surfactant interactions is to determine the change in surface tension of an aqueous surfactant solution when a small quantity of oil is added to the surface which contains a monolayer of surfactant. This gives the extent of oil adsorption into the tail region of the surfactant monolayer. A range of alkanes and surfactants will be discussed.

These studies at the air/water surface provide new insights into the solubilisation of oils into micelles i.e. curved monolayers.

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Thermodynamic relation of an insoluble monolayer at the oil/water interface and at the air/water interface in contact with oil

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Phospholipid monolayers of DPPC and DPPE are studied at three different types of interfaces: air/water, oil/water and air/water in contact with oil. The oils applied are hexadecane, dodecane and bicyclohexyl. The thermodynamic data for the fluid phase can be explained by a simple model explaining why the lateral pressures of the latter two interfaces basically differ by the spreading coefficient. Fluorescence microscopic observations reveal that the three interfaces can be prepared in pressure equilibrium exhibiting comparable phase sequences.

Sponsored by the Deutsche Forschungsgemeinschaft

INTERFACIAL STUDIES OF A BINARY SURFACTANT MIXTURE

John Hines

Unilever Research Port Sunlight Laboratory
Physical Chemistry Laboratory, Oxford University

The interactions in aqueous solution of mixtures of surface chemically pure Sodium n-Dodecyl Sulphate (an anionic) and n-Dodecyl-N,N-Dimethyl Amino Acetate (a zwitterionic) have been studied using measurements of surface tension and, following synthesis of deuterated species, by neutron reflection. Results of both sets of measurements indicate strong, non-ideal interaction between the two surfactants. The findings of these two techniques are compared and the limitations of a standard Regular Solution treatment in describing the observed behaviour is discussed.

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Experimental study of the breakage and melting of a two-dimensional crystal

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Laboratoire de Physique Statistique de l'E.N.S.
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We study monolayers of an insoluble amphiphilic molecule at the free surface of water. During the liquid-solid phase transition, we observe, by fluorescence microscopy, long rods of the two-dimensional solid phase. Shape being well adapted to micromechanical measurements, we have noticed that a rod, under the effect of a bending stress in the plane of the water, breaks after delay time. Statistics on the breakage time of such a crystal have shown, this time-lag breakage being a clearly defined function of the applied stress. For large deformations, a second mode of breaking coexists with the previous one: instantaneous breaking.

In addition, we have been interested in the effects of a prolonged bright light beam focused on a crystal. Illumination implies the nucleation of local volumes of liquid within the solid, leading to the process of melting. Our phenomenon seems to require the formation of impurities in the crystal, generated by the presence of oxygen in the air

**AN INVERSE MICELLAR CUBIC PHASE FORMED BY
PHOSPHATIDYLCHOLINE / FATTY ACID AND
PHOSPHATIDYLCHOLINE / FATTY ALCOHOL MIXTURES**

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An inverse micellar face-centered cubic phase, of space group Fd3m, formed by two series of fully hydrated diacyl phosphatidylcholine / fatty acid (PC/FA) and diacyl phosphatidylcholine / fatty alcohol (PC/FAlc) mixtures, with each lipid component having the same hydrocarbon chainlength, is reported in this work. This Fd3m phase occurs in PC/FA mixtures with chainlengths from C12 to C20 and in PC/FAlc mixtures with chainlengths of C14 to C20. All of the Fd3m-forming mixtures have a minor composition of PC with the PC mole fraction being 0.15-0.25. The Fd3m cubic phase is located between the inverse hexagonal H_{II} phase and the inverse micellar solution phase L₂. At chainlengths below C12 for PC/FA mixtures and C14 for PC/FAlc mixtures the H_{II} phase tends to be favoured over the Fd3m. The lattice parameter of the Fd3m phase increases with PC concentration and with chainlength.

HIGHLY ORDERED AGGREGATES IN DILUTE DYE-WATER SYSTEMS.

Gordon J. T. Tiddy*, Donna L. Mateer*, Andrew P. Ormerod*,
William J. Harrison† & Douglas J. Edwards‡

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Optical microscopy and X-ray diffraction measurements have been made on liquid crystals formed by two dyes in water. The dyes (cyanine dye figure 1 and azo dye figure 2) both form mesophases above ca. 0.2 wt. %. Low angle X-ray diffraction data show that the cyanine dye forms a layer phase, while the azo dye forms columnar nematic and hexagonal mesophases. For both dyes the aggregates appear to be rigid and well ordered. The thickness of the layers is equal to the width of one molecule, but the cross-section of the columns is equal to six times the dye molecular area. We propose a columnar pipe structure for these phases. The observation of multiple high angle X-ray diffraction peaks suggests that the molecules are well ordered at short range within the layers and columns. Hence the mesophases have high order at both the molecular and mesoscopic distance scale.

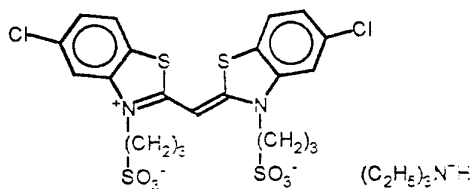


Figure 1: Cyanine Dye

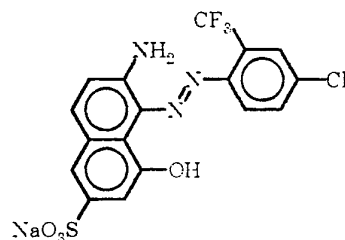


Figure 2: Azo Dye

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INVESTIGATIONS OF LIQUID CRYSTALLINE PHASES USING MICROSCOPY, DIFFERENTIAL SCANNING CALORIMETRY AND RHEOLOGICAL TECHNIQUES

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a. Zeneca Agrochemicals, b. Imperial College, London

Systematic studies of the phase diagrams of a series of nonionic surfactants namely Synperonic A7, A9, A11 and A20 are reported. The phase diagrams were first established using polarising microscopy, as a function of both concentration and temperature. For A7, a hexagonal phase was produced above 30% surfactant concentration which extended up to 55%. Above the latter concentration, a lamellar phase appeared. With A9, the appearance of the first liquid crystalline phase was shifted to higher concentrations but the phase diagram was qualitatively similar to that of A7. With A11, however, a cubic phase appeared between the hexagonal and lamellar phase. A20 showed a cubic phase as the first liquid crystalline phase (above 25%) followed by a hexagonal phase, but no lamellar structures could be detected. These transitions could also be followed using differential scanning calorimetry (DSC) and rheology. The phase diagrams were established using microscopy, DSC and rheology and good agreement was obtained between the three methods.

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Dynamic and Equilibrium Properties of New Sugar Surfactants.

Philippe Rogueda, Julian Eastoe: University of Bristol
Andrew Howe, Alan Pitt: Kodak

Sugar surfactants are believed to be a new alternative to petro-derived molecules. Being derived from renewable resources, their study is of paramount importance to the industry. This investigation of an homologous series of new sugar molecules aims to provide a new insight in the structural origin of surfactant properties.

These surfactants are made of two opened glucose rings, branched in the middle of a long hydrocarbon chain via amide linkages. Their originality not only lies in the location of the hydrophilic head groups but also on their very nature. The presence of several OH units and two hydrophilic chains opens up possibilities for intra and inter molecular hydrogen bonding.

We will review the equilibrium properties, CMC, thermodynamic parameters and phase diagrams as a function of hydrophobic chain length. Dynamic characteristics obtained with the Maximum Bubble Pressure apparatus will also be outlined.

This work is sponsored by Kodak Ltd.

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POSTERS

REVERSE VESICLES AS DRUG DELIVERY SYSTEMS

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It has been almost thirty years since the discovery that amphiphilic molecules, such as lecithin, could form approximately spherical, closed, bilayer structures known as vesicles (or liposomes) when dispersed in water. Since then these vesicular structures have been extensively investigated both as model biomembranes and more recently as drug delivery vehicles. Reverse vesicles (RV) in contrast have only recently been described in the literature. RV differs from normal vesicles in that the surfactant head groups and any associated water form the core of the bilayer while the hydrophobic tails of the surfactant remain in contact with the continuous organic phase. So far interest in RV has been mainly limited to their physico-chemical analysis and characterisation. The aim of this study is to examine these systems with a view to their use as a drug delivery vehicle in which polar or hydrophilic drugs can be delivered.

To date we have looked at the formation of RV in a range of surfactants and oils. Preliminary studies have involved constructing partial phase diagrams for the various oil and surfactant combinations. Various oils were studied including, hexane, dodecane, hexadecane, cyclohexane, toluene, isopropyl myristate and paraffin. The main surfactant used was Brij 30 ($C_{12}E_8$) although a number of other nonionic surfactants were also investigated. Areas of the phase diagram where a lamellar phase existed in equilibrium with an excess oil phase were identified as regions where RV could potentially be formed. The lamellar phase of these two phase systems was dispersed in the excess oil by means of sonication (bath or probe). The resulting one phase systems were examined for evidence of vesicle formation by light microscopy and light scattering studies. Of the oils studied, only toluene and cyclohexane failed to produce the relevant two phase system and were therefore not examined for RV formation. Relevant two phase systems, yielding RV were however identified in all of the other oils investigated, generally in the region where water and surfactant concentrations were similar and in the range of 7-25% by mass. Vesicle size as measured by photon correlation spectroscopy ranged from 200nm-1 μ m depending on the conditions of formation, that is bath or probe sonication.

Industrial Sponsor: Glaxo Research and Development, Park Road, Ware, Herts.

Comparison of Hyaluronan and Hylan Using Shear and

Extensional Viscosity Measurements

Saphwan Al-Assaf , P.A. Williams, J. Meadows, G. O. Phillips and S. Navaratnam, Centre of Expertise for Water Soluble Polymers, MRIC, NEWI, deeside, Clywd, CH5 4BR.

Abstract

Hyaluronan is a linear polymer found in bodily tissues such as skin, vitreous humour and synovial fluid. In the latter, hyaluronan viscosifies the fluid thus providing the lubricating function to the joint. One of the characteristics of rheumatoid arthritis is the reduction in the viscosity of synovial fluid. Despite its extremely effective use in ophthalmic viscosurgery, hyaluronan has been unable to meet all the clinical needs for viscosupplementation of diseased joints. For this purpose a series of modified cross-linked hyaluronans (hylan) of varying molecular weights have been prepared and their rheological characteristics investigated. In addition to shear flow studies, ~~the extensional~~ viscosity characteristics of the polymers have also been determined (using an opposing jet apparatus). The rheological differences between the polymers were found to be more pronounced in extensional flow with the extensional viscosity increasing dramatically with increasing concentration and molecular weight.

It is proposed that the measurements demonstrate that the hylan family provide more appropriate physical and mechanical properties for viscosupplementation of diseased joints, than the parent hyaluronan.

"SURFACE CHARACTERISATION OF METAL OXIDE PIGMENTS"

Rona L. Anderson, Faculty of Textiles, Heriot Watt University of Edinburgh

The co-operating body uses novel tints for biomedical purposes. The colouring materials in these inks are pigmentary metal oxides: red, yellow, brown and black metal oxides; titanium dioxide and cobalt chromium aluminium oxide.

There are a number of problems associated with these colouring materials, the most notable being the tendency to show colour separation in the ink film similar to that sometimes observed in paint films.

The project comprises physical characterisation of the pigments, especially by nitrogen gas adsorption, and technical assessment of the pigment performance. Some links have been found between the pigment particle aggregate nature shown by nitrogen gas adsorption isotherms and pigment behaviour in film.

Pilkington Barnes-Hind Ltd., Botley Green. Southampton.

THE ADHERENCE OF *PSEUDOMONAS AERUGINOSA* TO NOVEL BIOMIMETIC CONTACT LENS MATERIALS

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Biomaterials Research Group, Department of Pharmacy, University of
Brighton, Moulsecoomb. Brighton. BN2 4GJ *Natrtec, Brunel Science Park,
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Infection with *Pseudomonas aeruginosa* represents the most common clinical complication arising from the use of extended wear soft contact lenses and may lead to corneal ulceration. This study compares bacterial adherence to a standard 2-hydroxyethylmethacrylate lens with the novel phosphorylcholine containing Proclear® lens recently launched by Natrtec.

Lenses were incubated with 5×10^8 cfu mL⁻¹ of a clinical isolate of *Pseudomonas aeruginosa* (Moorfields Eye Hospital) in phosphate buffered saline on a shaking platform at 37°C for 3 h. Lenses were subsequently washed to remove any loosely adherent organisms, and examined using phase contrast microscopy. The percentage area of substrate covered by the bacteria was determined using image analysis (Perspective Instruments).

Table 1

Lens Type	Mean Surface Area Coverage $\pm$ SD
HEMA Lens (n=7)	31.9 $\pm$ 10.9%
Proclear® lens (n=6)	11.52 $\pm$ 8.36%

A significant reduction in bacterial adherence was observed for the Proclear lenses ($p < 0.01$, Mann-Whitney U-test) compared to the HEMA lenses (Table 1) suggesting that the PC containing material may reduce the risk of bacterial-mediated corneal ulceration.

Natrtec, a Division of Biocompatibles Ltd., Brunel Science Park, Kingston Lane, Uxbridge, Middlesex, UB8 3PQ.

ELECTROLYTE ELECTROREFLECTANCE STUDIES OF GOLD COLLOIDS

T Baum, M Brust, DJ Schiffrin

Department of Chemistry, University of Liverpool

Electrolyte Electroreflectance (EER) has been used for spectroscopical characterization of gold colloids which were deposited on a polycrystalline gold electrode, derivatized with 1,9 Nonanedithiol.

The EER signal obtained is shifted in phase and wavelength after derivatization and deposition of gold colloids. Potential and amplitude dependence will be discussed.

Stability Studies of Dispersions of Weakly Interacting Particles in Binary Solvent Mixtures

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Z. Kilrály, I. Dékány; Jozsef Attila University, Szeged, Hungary

Stability studies have been performed on hydrophobic and hydrophilic silica dispersions over a range of ethanol-cyclohexane binary solvent mixtures. Adsorption excess isotherms, rheology, SAXS (Small Angle X-ray Scattering) measurements and electrophoretic mobility measurements have been undertaken in an effort to explain the visually observed stability of the systems.

The thickness and composition of the adsorbed solvent layer on the surface of the particles has been determined from the adsorption isotherm using a multilayer adsorption model. This in turn has been used to calculate the attractive potentials between the particles as a function of solvent mixture composition. The stable / non-stable regions of the potential energy diagram have been compared with the Newtonian / non-Newtonian flow regions of the solvent composition profile which were obtained from rheological measurements. Electrophoretic mobility measurements have been made using PALS (Phase Analysis Light Scattering) apparatus to determine any electrostatic interactions in the systems. SAXS measurements have been used to study the floc structure in the aggregated dispersions.

Industrial Sponsor

Shell Research, Thornton Research Centre. Chester, UK.

THE SELECTIVE SEPARATION OF SOLUBLE SALT MINERALS USING A NON-IONIC FLOCCULANT

Samantha Beeson and Dr Colin Poole

University of Leeds

ABSTRACT

This paper describes the development of a novel technique for separating sylvite from synthetic potash by selective flocculation using a commercial non-ionic flocculant and an anionic dispersant. The possible adsorption and aggregation mechanisms present in the system are also discussed.

Results of initial flocculation performance tests undertaken on samples of pure sylvite, halite and water-insoluble minerals established the importance of a number of experimental parameters to be considered in the process. The data from these tests was then used to optimise conditions for recovering sylvite from a synthetic potash mixture having a similar composition to a typical ore, with separation being achieved at low dispersant and flocculant dosages.

THE EFFECT OF ELECTROLYTE ON THE PHYSICO-CHEMICAL PROPERTIES GELLAN GUM SOLUTIONS, A. M. Biffen, P. A. Williams and J. Meadows, Centre of Expertise for Water Soluble Polymers, MRIC, NEWI, Deeside, Clwyd, CH5 4BR.

Gellan gum is an extracellular polysaccharide which in aqueous solution exists as a disordered coil at high temperature but reversibly converts to an ordered helix on cooling. The conformational state of gellan gum is known to be a sensitive function of the ionic strength, the nature of the added counterions and temperature.

The effect of monovalent (KCl) and divalent (MnCl_2) electrolytes on the conformational change of gellan gum was assessed by monitoring the thermal and rheological properties of the gellan solutions using differential scanning calorimetry (DSC) and small deformation oscillation measurements. DSC cooling curves showed a single exothermic peak, with the setting temperature of the gels T_S increasing with an increase of KCl and MnCl_2 up to certain concentrations of electrolyte and then decreasing with further addition of salt. A similarly positioned maxima with respect to electrolyte concentration was also observed in the storage moduli of the systems.

Gellan gum solutions with excessive divalent cations were found to form strong thermoirreversible gels on cooling to below T_S which was quite different to the thermoreversible gels formed in the presence of monovalent cations. This suggests that the mechanism of gel formation in gellan with divalent cations is markedly different from that with monovalent cations.

FLUORESCENT LIFETIMES USED IN CRITICAL POINT WETTING STUDIES

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In investigating critical point wetting in the liquid mixture (n-heptane + perfluoro-n-hexane, $T_c = 43^\circ\text{C}$) at the quartz-liquid interface, the difference in the fluorescent lifetime of 1,6-diphenylhexatriene (DPH) τ_F in the solvents (n-heptane $\tau_F = 15$ ns, perfluoro-n-hexane $\tau_F = 32.5$ ns) has been exploited. The wetting film region can be probed by exciting the DPH with an evanescent wave. For $T < 31.4^\circ\text{C}$ the τ_F from evanescent wave excitation in the lower (perfluorohexane-rich) phase possesses the same value as the τ_F measured in the bulk lower liquid phase. For $T > 32.4^\circ\text{C}$ the τ_F from evanescent wave excitation in the lower phase corresponds to τ_F of the upper phase, whereas the τ_F of the bulk lower phase remains unchanged which indicates the presence of a wetting film of the heptane-rich phase at the quartz-liquid interface for $T > 32.4^\circ\text{C}$ and confirms the validity of this approach for investigating critical point wetting.

PREDICTING COMPLEX SURFACE CHANGES BY *IN VITRO* MODELLING

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Implanted medical devices present a surface for antibiotic-resistant biofilm development; maximum microbial adherence is achieved by organisms offering a surface chemistry and hydrophobicity optimal for biomaterial surface interaction. Growth rate and growth conditions significantly influence bacterial surface characteristics and attachment (Gilbert *et al.*, 1991).

Staphylococcus epidermidis is often found as a biofilm on continuous ambulatory peritoneal dialysis catheters (CAPD; Ludlam, 1991). During growth in pooled dialysis fluid surface hydrophobicity declined in early to mid exponential phase and returned to a maximum in stationary phase. In an *in vitro* CAPD model the complex interplay of temperature, gaseous tension, fluid replacement and compositional changes leads to a corresponding complexity in cell growth , hydrophobicity and adherence profile. An understanding of these phenomena may assist the optimisation of antibiotic and other control regimes.

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SUM-FREQUENCY SPECTROSCOPY OF TRI-CHAIN SURFACTANTS AND DODECANOL COADSORBED AT A HYDROPHOBIC SURFACE

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The applications of surfactants are diverse. Their ability to solubilise in water a variety of otherwise insoluble materials is critical in detergency as well as in the stabilisation of both macroemulsions and microemulsions. Despite their undoubted importance, the behaviour of surfactants at interfaces is poorly understood at the molecular level due to a lack of appropriate surface-analytical probes. Sum-frequency spectroscopy (SFS) is an excellent candidate for such *in-situ* studies. The capabilities of the technique are exemplified by our studies of the coadsorption of dodecanol and tri-chain surfactants from aqueous solution onto a flat hydrophobic surface. These mixtures were studied above and below the critical micelle concentration (cmc) of the tri-chain.

Below the cmc, coadsorption of the two surfactants occurs. At low concentrations of the tri-chain, the dodecanol displaces most of the tri-chain from the surface. At tri-chain concentrations just below the cmc, dodecanol simply adsorbs in the gaps around the tri-chain molecules, neither displacing the tri-chain molecules nor increasing their low conformational and orientational order. The corresponding order of the dodecanol is high in these films, just as it is in the absence of tri-chain. The tri-chain molecules are pictured as individuals or small clusters amid a "sea" of dodecanol.

Above the cmc and in the absence of salt, only the tri-chain adsorbs from the mixed solutions. However, if 0.1 M NaCl is added to these solutions, both tri-chain and dodecanol adsorb. The surfactant aggregates in salt-free solution are apparently able to completely solubilise dodecanol and so prevent it adsorbing to the hydrophobic surface. It is possible that salt reduces the curvature of the aggregates and effectively squeezes the dodecanol out into solution, from where it is able to coadsorb to the surface. This exciting result has initiated investigations into the adsorption from salt-stabilised microemulsions involving tri-chains.

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INTERACTIONS OCCURRING IN SUSPOSEMULSION

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My project is jointly sponsored by the University of Bristol and ICI. The aims of the project are to investigate the many variables which determine the physical properties of susposemulsions. Susposemulsions consist of three phases:- A dispersed oil phase (solvent + dissolved active ingredient) distributed in a continuous aqueous phase, producing an oil-in-water emulsion with a particle size of 0.5-3 μ m. The third phase is dispersed through the continuous aqueous phase. By using NMR self-diffusion measurements and neutron scattering it is possible to observe the interactions between the three phases. My present objective is to form the oil-in-water emulsion with a particle size between 0.5-3 μ m using an adapted Rapaport and Weinstock aerosol generator. The industrial relevance of susposemulsions are as formulations for pesticides.

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LIPASE-CATALYSED REACTIONS IN WATER-IN-OIL MICROEMULSION SYSTEMS.

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A number of enzymes have been solubilised in water-in-oil (w/o) microemulsion media and used to catalyse organic reactions such as ester synthesis/hydrolysis. Microemulsion-based organo-gels (MBGs) are systems formed by solubilising gelatin in w/o microemulsions yielding stable, transparent gels. Enzymes immobilised in MBGs provide a convenient means of reusing the biocatalyst and facilitates large-scale organic syntheses. Furthermore, these gels are highly reproducible in terms of their physiochemical properties, and allow molecular level dispersal of the enzyme.

The enzymes *Chromobacterium viscosum* (CV) and *Humicola lanuginosa* (HL) lipase have been solubilised in MBGs and w/o microemulsions in n-heptane. The lipase-containing MBG was used in the multigram synthesis of octyldecanoate from octanol and decanoic acid. With both enzymes, a high yield of ester was recovered of exceptionally high purity. CV lipase and HL lipase have also been solubilised in AOT stabilised water-in-oil (w/o) microemulsions containing octyldecanoate at R values ranging from 2 to 40 at 25°C. The extent of ester hydrolysis in each case was investigated in microemulsions containing either 0.020 mol dm⁻³ or 0.20 mol dm⁻³ octyldecanoate and the equilibrium reaction mixtures were analysed by capillary gas chromatography.

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STABILITY OF O/W EMULSIONS STABILISED BY AOT IN SYSTEMS
PREPARED FROM MICROEMULSIONS

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In microemulsion systems containing AOT (sodium bis-2-ethylhexyl sulphosuccinate) and heptane, the aggregates are oil-in-water microemulsion droplets in equilibrium with a pure excess oil phase at low NaCl concentrations (Winsor I). Around 0.05 M NaCl, 3 phase Winsor III systems are formed.

We have studied the stability of emulsions prepared from microemulsion + excess oil phases. The effect of electrolyte concentration was examined on the creaming and coalescence behaviour. Emulsion drop size distribution changes have been measured using a Malvern particle sizer, and the mobility of drops has been determined using microelectrophoresis.

The creaming rate of emulsions decreased initially as the electrolyte concentration increased. As the Winsor I/III boundary was approached, the creaming rate increased again. Water resolution was least around 0.035 M NaCl. Below 0.035 M, coalescence was absent but developed as the Winsor I/III boundary was approached. The initial radius of emulsion drops falls progressively with [NaCl] as the oil-O/W microemulsion interfacial tension decreases. The drop size changes are in the line with the stabilities of bulk emulsions. Zeta potentials of the drops are relatively high. They fall from ~ -100 mV at low [NaCl] to ~ -70 mV at 0.03 M NaCl and increase slightly approaching the Winsor I/III boundary.

THE MICROSCOPIC VISCOSITY OF BINARY LIQUID MIXTURES NEAR A CRITICAL ENDPOINT

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Evidence for anomalies in the microscopic viscosity of liquid mixtures near a critical endpoint where two phases merge (CEP) has been sought using fluorescence depolarisation. Near a CEP many quantities either vanish or diverge depending on the sign and magnitude of the critical index. Thus, since CEP viscosity η diverges weakly, the index y in the critical expression $\eta = \eta_0(T - T_c/T_c)^{-y}$ is small, 0.04. Although critical phenomena are macroscopic, and so almost never studied via molecular properties, critical behaviour is accessible at microscopic level via rotational correlation times τ_R obtainable from measurements of fluorescence anisotropy decay and related in turn to the rotational diffusion constant D via the Stokes-Einstein equation. $\tau_R = 4\pi\eta a^3/3kT = 1/6D$, (a is the hydrodynamic radius). Our measurements of τ_R suggest that the enhanced viscosity near a CEP can perhaps be detected by fluorescence anisotropy thus possibly opening up a new route to the study of criticality.

COMPETITIVE ADSORPTION OF SURFACTANT AND POLYMER AT THE AIR-WATER INTERFACE STUDIED BY NEUTRON REFLECTION AND SURFACE TENSION MEASUREMENTS

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Neutron reflection has been used in conjunction with deuterium labelling to study the adsorption and structure of polyethylene oxide (PEO) solutions containing caesium dodecyl sulphate (CsDS). The transition points in the mixed system were characterised by surface tension measurements with respect to the concentrations of polymer, surfactant and salt. The variation of PEO surface coverage was examined systematically using deuterated polymer and protonated CsDS. The polymer layer was almost completely replaced by surfactant at surfactant concentrations approaching the first transition point (T1). This corresponds to the onset of formation of polymer and surfactant micellar assemblies in bulk water. The surface coverage of surfactant was determined using deuterated CsDS and protonated PEO, (identical in molecular weight to the deuterated sample). Below T1, the area per surfactant molecule (A) was much higher than for the pure CsDS and the gap became smaller as T1 was approached. The difference indicates competitive adsorption of the surfactant and PEO and is consistent with the PEO surface coverage measurements in the mixed system. This also suggests that there is no enhancement in surfactant adsorption due to the presence of polymer in the dilute concentration range as observed for the PVP/NaDS system [1]. A was found to continuously decrease with surfactant concentration through T1, showing no particular correlation to the first transition point. The surfactant surface coverage in the mixed system approached its maximum value when the bulk concentration reached the second transition point, which corresponds to the onset of formation of regular surfactant micelles in the bulk phase [2].

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SYNTHESIS AND CHARACTERISATION OF FUNCTIONALISED
POLYPYRROLE-SILICA MICRO-PARTICLES.

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We have prepared surface-functionalised polypyrrole-silica micor-particles which should be excellent candidates as new "marker" particles in diagnostic assays.

The functionalised micro-particles have a surprisingly narrow partice size distribution and will thus be of interest as "model" colloids.

The optical density of the functionalised micro-particles is 2-4 times greater than that of commerical dyed polystyrene latex

The functionalise polypyrrole-silica micro-particles are made up of micro-aggregates of original silica particles. However the morphology is less "raspberry"-like than that of the unfunctionalised polypyrol-silica micro-particles. The conductivities of the functionalised polypyrrole-silica micro-particles are very low due to N - substitution of the polypyrrole.

ADSORPTION OF POLYISOBUTENYL-AZA-DICARBOXYLATE ESTER ONTO SILICA PARTICLES AND THE EFFECT OF TAIL GROUP ARCHITECTURE

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The diethyl azodicarboxylate derivative of mono-, di-, and tri- functional polyisobutylene has been synthesised at three molecular weights (M_n approximately 1000, 2000, and 3000 g mol^{-1} ; $M_w/M_n < 1.2$).

The adsorption properties of these polymers onto monodisperse spherical silica particles, of similar surface character to particles presently found within used engine oil (~100nm diameter, hydrophobic), in non-aqueous media has been studied by UV-Vis spectrometry.

Derivatives of polyisobutylenes are presently employed as additives in commercial engine oils to act as a dispersant of unwanted material. The aim of this research is to determine the role of the hydrocarbon tail group of these polymers in the dispersion activity, with a view to optimising the commercial and industrial uses.

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NEUTRON REFLECTION STUDIES ON ADSORBED POLYELECTROLYTE BLOCK COPOLYMERS

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Neutron reflection data on an aqueous system of poly(methyl methacrylate)-poly(methacrylic acid) (PMMA-PMAA) block copolymers, adsorbed onto silicon, at varying pH's will be presented. The small PMMA block acts as an anchor with the PMAA polyelectrolyte block trailing out into solution. Studies on a single plate indicate that the adsorbed layer expands as the pH rises above the pK of the acid group. This is due to the increased interchain repulsion as the charge density on the buoy blocks increases, assuming that this does not result in any desorption.

The same system will also have been studied on the new surface forces apparatus developed and recently improved in Bristol. This apparatus allows the use of neutron reflectometry to study the effect of compression on two parallel polymer layers. These results will give both the structure of the compressed polymer layer and information on the forces between the two polymer layers.

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SOLUBILISATION OF OILS BY SURFACTANTS

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Oils which are normally insoluble in water can be *solubilised* with the aid of a suitable surfactant. Solubilised oils are contained in aqueous solution within the oily interiors of surfactant aggregates. The overall aim of this project is to gain a deeper understanding of the factors which determine the extent of solubilisation.

We have investigated how the *shape of the initial micellar aggregate* affects oil solubilisation. Sodium dodecyl sulphate (SDS) and alkyltrimethyl ammonium bromide (C_n TAB) surfactants form small spherical micelles at low concentrations of an added salt but the micelles grow to long rods at a critical salt concentration. The solubilisation of heptane in SDS micelles increases steadily with increasing [NaCl] with no abrupt changes at the salt concentration corresponding to the transition from spherical to rod micelles. In contrast, solubilisation curves for C_n TAB surfactants do show abrupt changes. The results are discussed in terms of the locus of solubilisation.

Acknowledgement.

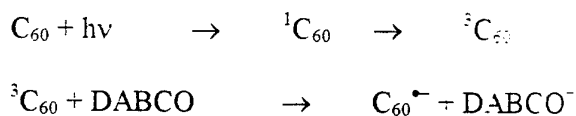
We thank the University of Hull for provision of a Graduate teaching Assistantship for DC.

Studies of Aqueous Suspensions of Carbon-60

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Since the discovery of Carbon-60, research into the chemistry of this fascinating molecule has been limited by its insolubility in aqueous media. One method of solubilising C₆₀ in water is via its incorporation into surfactant micelles where C₆₀ is stabilised as colloidal aggregates. Various non-ionic surfactants have been used as the solvent in this work. Small Angle Neutron Scattering and UV-visible absorption spectroscopy have been used to probe the structure of these systems. The dependence of C₆₀ concentration and the role of surfactant structure on the size and stability of the aggregates has been investigated. The photophysical properties of C₆₀ incorporated into these micelles has also been studied. The addition of triplet quenchers such as 1,4 - diazabicyclo (2.2.2) octane (DABCO) may be added to decrease the triplet life time of C₆₀ and yield the radical anion, C₆₀^{•-}, as shown below:-



REMOVAL OF STARCH BASED DEPOSITS FROM STAINLESS STEEL SURFACES USING CHEMICAL CLEANING AGENTS

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A kinetic evaluation of potato starch removal from stainless steel using a range of chemical cleaning agents is presented. The deposit produced exhibited both a high soil-soil and soil-substrate bond strength, thus representing a tough cleaning problem. The existence of an optimum temperature for cleaning potato starch was found at 50°C using sodium hydroxide and nitric acid. The results also indicated a concentration optima of 14 wt% when using sodium hydroxide. Cleaning removal time was found to be a strong function of temperature when using the alpha-amylase enzyme (BAN).

The design and construction of experimental apparatus is being undertaken to enable the production of a reproducible deposit which can be subsequently cleaned under controlled thermo-hydraulic conditions. The cleaning kinetics of the process will be studied using two techniques: measuring the starch remaining on the surface (gravimetric); quantifying the starch dissolved in the effluent stream using TOC (Total Organic Carbon) measurement.

Behaviour of asymmetric di-chain dimethyl ammonium bromides

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In order to determine the specific contribution of the hydrocarbon chain volume: V_s and structure on properties of surfactants at oil-water and air-water interface, we prepared a range of new pure dialkyldimethylammonium halide surfactants where the structure of the two chains is varied separately and systematically, $C_{12}H_{25}C_nH_{2n-1}N(CH_3)_2Br$ where $n=4,5,6,7,8,10,12,14,16,18$.

The liquid crystal and microemulsion phase behaviour has been investigated using a hot-stage polarising microscope and ocular observation. When $n \geq 5$, the liquid crystal behaviour looks like that of single chain ($C_{16}TAB$), $L_2-H_I-C-L\alpha$. For $n \geq 6$ no phase boundaries appear, but two types of $L\alpha$ are present, this was confirmed by NMR ^2H quadrupolar splitting.

SANS studies of w/o systems ($n \geq 10$) showed that the reverse micelle shape changes from cylinder to sphere as the water content increases. The phase behaviour of water-surfactant-cyclohexane shows for $n = 10, 12$ re-entrant microemulsion form. For $n > 12$, the larger the second chain the wider the range of stability of the microemulsion.

SBFSS

ADSORPTION OF SHORT CHAIN PHOSPHOLIPIDS AT AIR/WATER AND OIL/WATER INTERFACES

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As a preliminary to a detailed investigation of the relationship between phospholipid monolayer properties and the stability phospholipids confer on emulsions, we have studied the adsorption of dihexanoyl and diheptanoyl phosphatidylcholine and dihexanoyl phosphatidylethanolamine at air/water and alkane/water interfaces. Since equilibrium surface and interfacial tensions are attained rapidly we have used the drop volume technique (a dynamic method) for the determination of tensions. The method is well-suited to systems where only small volumes of solution are available. From tensions obtained over wide ranges of concentration it has been possible to (a) obtain standard free energies of adsorption from solution into dilute monolayers, (b) explore the applicability of various surface equations of state to phospholipids in fairly dilute monolayers, (c) measure critical micelle concentrations (cmc's) and (d) determine areas per molecule in close-packed monolayers. Cmc's and molecular areas are required for the study of emulsion stability conferred by phospholipids.

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RHEOLOGY OF POLYSACCHARIDE GELS

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An investigation into the rheological properties of certain polysaccharide gels has been carried out. The polysaccharide gels investigated were Xanthan and κ -Carrageenan gels. Rheological parameters investigated were viscosity, viscoelasticity, and gel strength. The effect of change in temperature, presence of salt and of suspended particles on these rheological parameters were also investigated. Preliminary results show that both gels are shear thinning with pronounced yield values in the concentration regimes investigated. The rheology of Xanthan was fairly stable to changes in temperature while that of κ -Carrageenan showed phase separation behaviour in the temperature range investigated. The Dougherty-Krieger equation was tested when the gels were loaded with ballotini particles and a reasonably good fit was obtained with Xanthan gels.

A MICROSCOPIC APPROACH TO THE MECHANISMS OF AGGLOMERATION

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Agglomeration can be defined as the action of gathering particulate matter into a mass. This project focuses on the formation and rupture of pendular liquid bridges between particles in "wet" agglomerates. In particulate dispersions the presence of a binder solution causes liquid bridges to be formed between particles, which are then held together by the surface tension at the liquid / air interface and the hydrostatic suction pressure in the bridge.

As there is a lack of experimental data for particles attached by liquid bridges, especially particles below 10 μ m in diameter, a microscopic approach has been adopted here. Thus the experimental equipment consists of a microscope connected to an image analyser, with force transducers mounted to its stage which enable the forces required to rupture bridges between particles to be measured.

It is intended to use the results to develop a more rigorous understanding of the fundamental mechanisms of agglomeration and to produce a predictive model which is universally applicable and not system specific.

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KINETICS AND MECHANISM OF THE HYDROLYSIS OF PRIMARY ALKYL SULPHATES IN AQUEOUS COLLOIDAL SOLUTION.

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Kinetic and mechanistic aspects of the hydrolysis of primary alkyl sulphates (PAS) in aqueous solutions containing up to 70% PAS by weight have been studied. Initial experimentation on sodium dodecyl sulphate (SDS) has been extended to sodium 2-methylundecyl sulphate. Aqueous solutions of such compounds are known to form lyotropic liquid crystalline phases at high concentrations.

PAS's apparently hydrolyse by two distinct pathways, a slow uncatalysed route observable in neutral solutions, and a more rapid acid catalysed process. Rates of both processes vary in a complex manner with surfactant concentration. Autocatalysis by the product sodium bisulphate has been shown to occur, and specific hydrogen ion catalysis applies for SDS hydrolysis. ^{18}O -labelling experiments have been carried out to provide further insight into the reaction mechanism of PAS hydrolysis.

Phase studies of aqueous PAS solutions have been carried out in an attempt to relate reaction rates to the nature of the aggregates present in solution.

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THE STUDY OF LUBRICANT ADDITIVES ONTO SOOT USING A QUARTZ
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The production of soot during engine use, leads to an undesirable increase in viscosity of the lubricating oil. This can be reduced by the effective dispersion of the soot by additives present in fully formulated lubricants. The dispersion is a poorly understood process, although it is certain that the adsorption of ashless dispersant molecules onto the soot is required.

This work concentrates upon the behaviour of the various component additives, separately, and in synergic combination as well as that of model compounds that mimic selected aspects of these components.

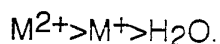
Using the QCM, changes of frequency can be detected in real time, from which adsorbed mass changes in the order of nanograms per unit area can be calculated. Research to date has concentrated on the adsorption of well characterised surfactants, which model the various additives, onto a carbon coated crystal.

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NOVEL FOOD GELS. P. Fitzpatrick, P. A. Williams and J.

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Xanthan gum is a naturally occurring anionic bacterial exopolysaccharide which when mixed with konjac glucomannan forms strong thermoreversible gels due to polymer association¹. The addition of various electrolytes and the effect of mixing ratios were studied rheologically and thermally. It was found that strong gels form even if the amount of xanthan gum was in excess of 90%. At these ratios the storage modulus (G') measured by small deformation oscillations at 15°C decreased in the order:-



This is the reverse trend to that observed for 1:1 mixtures². This suggests that there is a different mechanism of binding in water and electrolyte. The results are interpreted in terms of the equilibrium position of the order to disorder conformational transition of xanthan gum which is sensitive to the addition of electrolytes.

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CRYO-ESEM : A NOVEL APPROACH TO ICE-CREAM

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Conventional SEM requires extensive preparation of samples due to the high vacuum required in the observation chamber. This is not a convenient way to view ice-cream and other such dairy products; potentially, much of the structure can be lost and artefacts produced during preparation. However, Environmental SEM (ESEM) uses a differential pumping system to allow a chamber pressure of between 0.1 and 40 torr. This ability of ESEM eliminates the need for damaging preparation procedures. Reported here is a cryogenic adaptation of ESEM - cryo ESEM - to investigate the microstructure of ice-cream, and how beam etching can reveal the morphology of crystalline structures.

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UNDERSTANDING SCRAMBLING IN LANGMUIR-BLODGETT FILMS USING NEUTRON AND X-RAY REFLECTION.

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Many applications of Langmuir-Blodgett films (eg. pyroelectric and non-linear optical effects) require alternating layers of two complementary molecules. The properties of these films are often disappointing and in some cases this is thought to be due to partial intermixing of successive layers during the deposition process. We have therefore used neutron and X-ray reflection to investigate the correlation between the degree of intermixing and the deposition conditions for LB films of both simple and more complex molecules, using deuterium-labelled layers. Eight experimental parameters have been varied independently and their effect on the distribution of the labelled molecules within the multilayer structure is being studied. Results so far indicate that the most important factor which must be considered whilst dipping is the fluidity of the monolayer at the air-water interface. This and other results will be discussed in more detail, with the aim of establishing the best experimental conditions for successful dipping of alternating LB films.

INITIATION OF AGGREGATION OF SURFACE COLLOIDS

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Aqueous suspensions of latex microspheres at air-water interfaces are very useful to model various processes in physical systems including aggregation [1]. Earnshaw and others [2], have found that latex particles of sizes from 0.8 to 3 microns placed on a water surface form very stable monolayers with a crystal like structure which aggregate only on the addition of electrolyte or surfactant solutions at an air-water interface. Contrary to this, Williams and Berg [3] found that latex particles at an air-water interface aggregate without the need for electrolyte or surfactant. Evidently, the mechanisms of the confinement of a monolayer at such interface are not entirely understood.

In this paper, an experiment is described which helps elucidate the mechanisms of confinement and upholds the claim made by Robinson and Earnshaw [4], that colloidal particles are negatively charged at the air-particle interface. Very stable monolayers of latex microspheres of size range one to three microns were formed. It was found that when positive ions were fired at the monolayer (using a Zerostat gun), aggregation occurred very rapidly. Similar effects were observed if the monolayer was exposed to ultraviolet light. The physical effects underlying the discrepancy between the experiments will be discussed.

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Stability of Sodium Caseinate Containing Oil-in-Water Emulsions

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Sodium caseinate is a well known food emulsifier. Recently it has been shown that, for oil-in-water emulsion systems using tetradecane, sodium caseinate concentrations above the maximum droplet surface coverage can have a noticeable effect on the emulsion stability. Ultrasonic and rheological techniques have been used to study this effect. At low oil phase concentration (10 wt% tetradecane) caseinate concentrations above 2.5 wt% caused enhanced flocculation. At medium oil phase concentration (35 wt% tetradecane) enhanced flocculation was observed above 3 wt% protein with increases in the low shear viscosity of the emulsion being observed at 5 wt% and 6 wt%. At high oil phase (45 wt%) enhanced flocculation was observed at 4 wt% and 4.5 wt% but not at 5 wt% or 6 wt%. There was also a significant increase in the low shear viscosity at 5wt% and 6 wt% protein. Further rheology and creaming experiments with emulsions containing Tween 20 as well as the protein have showed that unbound sodium caseinate is the likely cause of this effect and that the mechanism is some form of depletion flocculation.

BBSRC - Swindon, Wilts

**CONTACT ANGLE MEASUREMENTS DURING LANGMUIR WETTING:
A NEW METHOD TO QUANTIFY THE MOLECULAR ADHESION INTERACTIONS
AND THE TRANSFER RATIO**

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In Langmuir wetting a monolayer covers both, the aqueous subphase and the submerged solid substrate. The equilibrium contact angle in this configuration can be used to determine the transfer ratio and the adhesion energies between the monolayer and the substrate. Both quantities are measured for different Langmuir monolayers and substrate surfaces as function of the molecular packing.

For the phospholipids DMPE and DPPC and Si/SiO_x-substrates the transfer ratio depends on the monolayer phase and reveals substrate-induced phase transitions. These are shifted to lower surface pressures compared to the coexistence pressure of the isotherms. The contact angle measurements agree with fluorescence microscope studies.

The molecular adhesion energies are in the range between 0.8 - 4.0 kJ/Mol (= 0.33 - 1.6 kT/molecule at 293K). These values depend on the molecular packing and are highly sensitive to the substrate surface preparation.

INVESTIGATING SURFACE INTERACTIONS INVOLVING CLAYS, AQUEOUS SALT SOLUTIONS AND POLYALKYLOXIDES

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The aim of my project is to investigate the surface and near-surface interactions involving clays, aqueous salt solutions and polyalkyloxides. The presence of aqueous salt solutions and polyalkyloxides breaks up the naturally occurring hydration layers of water that surrounds suspended clay particles. Clays are layer lattice silicates that form a characteristic "house of cards" structure that leads to the occurrence of both internal and external hydration layers. When polyalkyloxides disrupt the internal hydration layers they reduce the clays swelling in an aqueous environment. Different aqueous salt solutions aid this disruption to a greater or lesser degree. The mechanism behind this disruption is not known. NMR is an ideal technique for probing the clay surface to find out exactly what conformation the polyalkyloxides adopt at the clay surface. Small angle neutron scattering will be used to determine the volume fraction profile of the adsorbed polyalkyloxides near the clay surface. Between these two techniques it is planned to determine the conformation of the polyalkyloxides at the clay surface and the role of the aqueous salts in order to provide a mechanism for this interaction.

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ANALYSIS OF SEDIMENTING KAOLIN SUSPENSIONS BY ELECTRICAL RESISTANCE TOMOGRAPHY

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Suspended kaolin particles exhibit a propensity for orientation along the shear gradient when flowing through narrow-bore pipes. Stopping the flow causes the particles to randomise their orientation under Brownian motion, and then sediment. These principles can be observed by axial electrical conductivity measurements along the pipe. It is intended to extend this by utilising miniaturised Electrical Resistance Tomography (ERT) measurements to thereby obtain a cross-sectional resistivity profile of the dispersion. Time analysis of this profile should enable particle sizing and aspect ratio predictions.

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FORMATION OF MINIEMULSIONS BY PHASE SEPARATION

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The settling of emulsions is often related to the drop diameter, and a common practice to increase the emulsion stability is to produce extremely fine droplets, down the sub-micron range. In most practical cases it is quite difficult to attain such a size by stirring, and an attractive and alternative method is the phase separation which is described in the present work.

Surfactant-oil-water systems containing nonionic species exhibit a phase behaviour that depends upon many formulation variables, which include the temperature. It is shown that by cooling a stirred ternary system from above to below the optimum temperature at which a three-phase system is exhibited, a dispersed system is formed containing extremely fine droplets ($<1\mu\text{m}$), from which we give the name miniemulsion. The process is explained in terms of the kinetics of the phase separation phenomena, when the formulation undergoes the Winsor II $\rightarrow$ III $\rightarrow$ I transition.

ESTIMATION OF THE PEG CHAIN LAYER OF LPLA-PEG PARTICLES USING VISCOELASTIC MEASUREMENTS

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A range of biodegradable polylactide-polyethylene glycol (PLA-PEG) AB block copolymers have been produced for use as drug delivery systems. These copolymers form particles with PLA in the core surrounded by hydrophilic PEG chains in aqueous media. The thickness of the PEG layer, which controls the stability and biological interaction of the particles, has been estimated for LPLA-PEG from the viscoelastic properties of the system.

Strain and frequency sweeps performed for several volume fractions, ϕ , indicated a typical viscoelastic system, with the storage modulus, G' , becoming greater than the loss modulus, G'' , as ϕ increased, indicating PEG chain interaction. The critical volume fraction, ϕ_{eff} , (where overlap of the PEG chains commences), together with the hydrodynamic radius of the particles (from photon correlation spectroscopy), gave a PEG chain length of 6.4 nm.

This method, to accurately estimate the hydrated PEG chain layer, will allow a greater understanding of the role of PEG in drug targeting.

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CHARACTERISATION OF NON-AQUEOUS LYOTROPIC LIQUID CRYSTALS

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Ammonium perfluoro-octanoate (APFO)/ water mixtures have long been known to produce well defined liquid crystalline phases. The effects on the phase behaviour caused by replacing water with ethylene glycol has been investigated using optical microscopy, laser Raman spectroscopy and ionic conductivity. The main differences observed due to the substitution are, firstly, the lack of a nematic phase, secondly, significantly lower transition temperatures and finally, a marked increase in the cmc. At intermediate mixtures of water and glycol no liquid crystal phases are observed. A rational for the observed phase behaviour is offered.

SIMULATED 2-D COLLOIDAL AGGREGATION

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The structure of a system of aggregating particles is studied by simulation in two dimensions, using an on-lattice diffusion limited cluster aggregation model. The dynamics and kinetics of the aggregating system compare very well to those found from experiment [1]. We calculate the static scattering function $S(Q)$ for the system and have found that the random aggregation process spontaneously produces symmetry. In particular, in the late, rapid stages of aggregation the two dimensional scattering function $S(q_x, q_y, t)$ displays a six-fold structure. The time scaling properties of $S(Q)$ are examined. The peak in the scattering function, reported for many experimental aggregating colloidal systems and observed in the simulated structures, is shown to scale as $S(q/q_m, t) \propto q_m^{-d_f}(t)F(q/q_m)$ [2,3]. We have also shown from $S(Q)=P(Q)A(Q)$ (where $P(Q)$ is the effective form factor and $A(Q)$ is the structure factor of the centres of gravity of the clusters in the system) that both $P(Q)$ and $A(Q)$ also scale. We examine various characteristic length scales in the model system, such as the average radius of gyration of clusters, the average separation of clusters and the length scale equivalent to the position of the structure factor peak in an attempt to determine whether the system can be characterised by a single length scale.

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MICROEMULSION FORMATION BY SYNTHETIC AND NATURAL PHOSPHOLIPIDS

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I am working as part of a programme to understand the behaviour of phospholipids at oil-water interfaces with particular reference to microemulsion phase equilibria.

Microemulsions are self assembly systems that have important applications, for example in biotechnology and enzymology. But any large scale application, either in the research laboratory or in industry, has been severely hindered by the use of biologically harmful surfactants and hydrocarbon oils. It is hoped that new microemulsion systems formed by biologically compatible phospholipid surfactants and oils can be developed.

Preliminary work is being done on the characterisation and phase stability of various phospholipid/ hydrocarbon/ water systems. Small-Angle Neutron Scattering will be used to reveal the structure within the microemulsion phases and Surface Laser Light Scattering to measure the ultra low interfacial tension in these systems. Recent results from these preliminary studies will be presented.

RHEOLOGY OF HEAT-SET PROTEIN-STABILISED EMULSION GELS: INFLUENCE OF NONIONIC AND ANIONIC SURFACTANTS

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Small-deformation oscillatory shear measurements were made on heat-set emulsion gels (5–8 wt % β -lactoglobulin, 38 wt % *n*-tetradecane, pH 7) containing a low-molecular-weight surfactant—nonionic Tween 20 or anionic SDS. The emulsions containing the surfactants added prior to heat treatment were gelled *in situ* by heating the concentric cylinder rheometer cell to 90 °C for 30 min, followed by cooling to 30 °C. Storage and loss moduli and protein surface coverages of the emulsion gels were determined over a range of surfactant/protein molar ratio R . The emulsion gel strength was found to be sensitive to both surfactant/protein ratio and protein content. In emulsion gels containing Tween 20, the storage modulus was shown to increase at low surfactant concentrations ($R \approx 1$), to decrease at intermediate surfactant concentrations ($R \approx 2$), and then at high surfactant concentrations ($R \geq 4$) either to increase again or to remain low, depending on the protein content. Similar trends were observed with emulsion gels containing SDS but only at higher surfactant concentrations (*i.e.* $R \geq 4$). In particular, the surfactant concentration at which a decrease in the storage modulus was observed corresponded to the point where there was a substantial reduction in the protein surface coverage in the presence of the same surfactant. The rheological behaviour of the emulsion gels could be explained in terms of interfacial and bulk protein–surfactant interactions and protein competitive displacement from the interface.

SEPARATION OF CALCITE AND DOLOMITE FROM APATITE BY MAGNETIC COATING

Ruozhou Hou

Institute: Camborne School of Mines

Supervisor: Prof. R. A. Williams

University of Exeter

Preliminary tests have been conducted to explore the feasibility of separating calcite and dolomite from apatite by means of magnetic coating. The effects of magnetite additions, sodium oleate concentrations, particle size, conditioning time, and the zeta-potentials of the minerals on the magnetite coating have been investigated. The results show that the selective coating of magnetite on calcite and possibly dolomite can only be achieved using low concentrations of sodium oleate. Since in this case only a very small proportion of magnetite added to the suspension is actually involved in coating, resulting in the bulk magnetic susceptibility of the aggregates too low to be captured by the low intensity magnetic field, the only possible way to achieve successful separation of calcite and dolomite from apatite in case of magnetic coating is to use high intensity or high gradient magnetic separators which can exert a much stronger magnetic force on the weakly magnetic aggregates.

INVESTIGATING THE POTENTIAL CAPILITIES OF ANIONIC/NONIONIC SURFACTANTS IN MICROEMULSION EOR PROCESSES

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Arshad Hussain, Paul F. Luckham and Th. F. Tadros

Microemulsion flooding is considered to be one of the major chemical processes designed for enhanced oil recovery. Ultra-low interfacial phenomena play an important role in the design of microemulsion process and recovery of residual oil trapped in reservoir pore spaces. Substantial work has been done on the physicochemical aspects of the phase behaviour of microemulsion systems containing petroleum sulfonates. **High salinity, high divalent cation contents, high adsorption, oil type and high temperature** are major adverse conditions present in many reservoirs which make microemulsion flooding ineffective.

Literature on the phase behaviour of anionic surfactants, specially on the petroleum sulphates and sulphonates, reveals that surfactant partitioning in oil/water/surfactant system is very sensitive to the electrolyte concentration. When comparing the phase behaviour of pure nonionic surfactants, it has been found that the nonionic surfactants with polyoxyethylene chain as the hydrophilic head group exhibits a relatively high tolerance to salinity and divalent cation contents but a poor tolerance to temperature. In contrast to this the anionic surfactants show higher stability to temperature changes but is sensitive to the salinity. The problem arises when a system is to be optimized with high salinity (5-25 grams/decilitre) and exhibit acceptable tolerance to temperature changes.

The purpose of this study is to elaborate the issue of whether nonionic in conjunction with anionic surfactants can be used to design an optimum microemulsion slugs. These can result in an ultra-low interfacial tension, insensitivity to high salinity and temperature, acceptable adsorption (retention) and are effective in the recovery of the residual oil saturation in petroleum reservoirs.

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HETEROFLOCCULATION IN PARTICULATE COLLOIDAL DISPERSIONS

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Heteroflocculation is the study of the stability of colloidal dispersions containing dissimilar particles. The stability of these types of systems is affected by the interactions which occur between the particles, and dictates whether particles remain as discrete entities or become aggregated and therefore destabilised. Theories based on the DLVO theory are being developed to explain the interactions, as the current model is insufficient to fully define the interactions between dissimilar particles.

Heteroflocculation studies involving the interactions between thermosensitive colloidal microgels of poly(N-isopropylacrylamide) and an oppositely charged polystyrene latex will be reported. Dispersions of this mixed particle system are stable at room temperature but undergo an aggregation upon heating at low concentrations but remain stable at higher additions. The results are described in the context of a charge reversal mechanism.

THE ROLE OF ZETA POTENTIAL IN DISSOLVED AIR FLOTATION

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The application of surface science concepts has gained increasing importance in the understanding of solid-liquid separation phenomena. Although electrokinetic parameters have been known to exist for considerable time, their application has been limited due to the difficulties of reliable measurement.

The usefulness of such information will be demonstrated with particular reference to the dissolved air flotation process. The effects of surfactants and electrolytes on the surface properties of clay minerals will be presented illustrating the relevance these have on the process.

This data forms part of a current EPSRC funded project into the fundamentals of the removal mechanisms.

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SURFACE WAVES ON SURFACTANT SOLUTIONS

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The absorption properties of surfactant solutions are of considerable scientific and commercial interest. Established theories predict the effects of these properties upon surface wave behaviour [1]. However, recent work [2,3] using surface laser light scattering (LLS) to study the dispersive behaviour of thermally excited capillary waves (CWs) on the surface of aqueous solutions of anionic [SDS] and cationic [CTAB, DTAB] surfactants has revealed departures from the predictions of these models. At high concentrations and relatively low [$\leq 10^5 \text{ s}^{-1}$] frequency the wave propagation is as expected. However the propagation departs from expectation at low concentration ($\leq 1/10 \text{ CMC}$) and higher frequency [$\geq 3 \times 10^5 \text{ s}^{-1}$]. This work suggests the presence of a potential barrier to adsorption at the surface which appears to act to reduce the stability of the dilational surface waves which are coupled to the CWs observed by LLS. The surface viscoelastic properties inferred from the LLS data are fully in accord with the suggestion that the dilational waves are of reduced stability.

We present here the results of a similar set of LLS experiments on aqueous solutions of zwitterionic [hexadecyl dimethylammonium propyl sulphonate] and nonionic [pentaethyleneglycol mono n-decyl ether] surfactants designed to probe such behaviour. The results clearly indicate the likely role of electrostatic effects in the adsorption barrier.

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EFFECT OF SURFACE MODIFICATION ON THE RHEOLOGY OF CONCENTRATED DISPERSIONS.

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Rheological methods are commonly used to determine the properties of pastes. The rheology can be used as an analytical tool to determine the optimal operating condition of a unit operation, e.g. the optimal amount of dispersant, from the measurement of the viscosity vs. the amount of dispersant used. Rheological measurements are also used for quality control in order to minimise the batch to batch variation before a paste (e.g. in ceramic industry) is process further.

The rheology of a "pasty" system is primarily dependent upon the operating interaction forces between the particles. A change in the magnitude as well as in the nature of the interaction forces will change the rheology of the system. The interaction forces between the particles can be changed by the surface modification of the particulate material by surfactant/polymer grafting/adsorption and/or by changing the pH of the continuous phase. If the particulate material has a positive or negative charge, there is a net electric repulsion between the particles and the particles tend to repel each other. If there is no charge on the surface of the particulate material, there is no net electric repulsion between the particles, and the particles can come close to each other. When there is a zero or a low electric charge on the particles, the viscosity and the yield stress are high when compared with the viscosity and the yield stress of the particulate material bearing more positive or negative charge on the particles.

The purpose of this present work is to examine the effects of the surface modification of particulate materials on the rheology of the concentrated dispersions/pastes. The surface modification can be achieved by grafting polymer chains or adsorbing polymer/surfactant molecules on the surface of the particulate material. The rheological studies can be carried out using different methods now established in the literature e.g. extrusion, indentation, upsetting etc. The rheological properties are then extracted from the quantities measured and incorporated into a suitable rheological model (constitutive equation) which must also include a description of the boundary conditions.

Ministry of Science and Technology, Government of Pakistan

CO-ADSORPTION OF t-BUTANOL AND n-PENTANOL AT THE AIR/WATER INTERFACE

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Surface tensions of aqueous solutions containing varying concentrations of either single or mixed alcohols were measured using the Pendant Drop technique. Computer analysis was used to obtain the coordinates of the drop profile directly from a video image. The Selected Plane method was applied to these data points by fitting spline functions at the equatorial position and at the position of the selected plane.

Mixtures of two amphiphiles adsorbing from dilute aqueous solutions produce surface tensions which depend on their interactions at the interface. t-Butanol and n-pentanol were chosen for study because their limiting surface areas are determined by the alkyl groups. Data relating to the co-adsorption of the two alcohols from mixed solutions have been used to test the validity of the regular solution theory in describing the properties of the mixed surface phase.

MEASUREMENTS OF SHEARING FORCES USING A MODIFIED SURFACE FORCES APPARATUS

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Friction occurs between surfaces in close proximity when they slide past each other. It is primarily due to molecular interactions between the surfaces. Interface asperities normally complicate the interpretation of these data.

We have modified a form of the surface forces apparatus to simplify the friction experiment by removing the effect of asperities. The apparatus uses molecularly smooth mica surfaces on which polymeric layers are adsorbed. In this new apparatus the upper mica surface moves parallel to the lower mica surface at constant known separation. Shear is generated by application of a voltage across a piezoelectric bimorph attached to one surface, and the transmitted motion is detected by using a second bimorph. A refinement of the method involves applying an AC voltage to the piezoelectric bimorph, and hence the viscoelastic shear properties of the adsorbed layer can also be investigated. The classic frictional stick-slip response is observed with the DC voltage. We have studied surfactants (phospholipids deposited on the mica surface), and it has been observed that these surfactants lower the friction.

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SYNTHESIS AND CHARACTERISATION OF MICRON-SIZED, POLYPYRROLE-COATED POLYSTYRENE LATEXES,

S.F. Lascelles and Dr S. P. Armes. University of Sussex.

Wiersma *et al*¹ at DSM Research have demonstrated that sterically-stabilised latex particles can be coated with a layer of polypyrrole in aqueous media to form conducting polymer latexes which exhibit good colloid stability. The conducting polymer is formed as a thin layer at the surface of the latex particles without significantly affecting the steric-stabilisation of the particles by the non-ionic polymer. The Dutch group have focused on coating various low T_g latexes of sub-micron dimensions.

We have demonstrated² that sterically-stabilised polystyrene latex particles in the micron size range can be coated with a layer of polypyrrole in aqueous media to form conducting polymer latexes. The synthesis conditions can be varied in order to control the conducting polymer loading in the final composite particle. We have extensively characterised these particles using a variety of techniques, including: scanning electron microscopy, disc centrifuge sedimentometry, API aerosizer, infrared spectroscopy and microanalysis.

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PREPARATION OF ROSE BENGAL LOADED ALBUMIN NANOSPHERES

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Human serum albumin (HSA) and methoxyl polyethylene modified HSA (HSA-mPEG) nanospheres with a size about 100 nm in diameter were prepared. Rose bengal (RB) as a model drug was incorporated into the particles during the particle production or by post-adsorption. The drug incorporation was affected by the different production method and the different structure of HSA and HSA-mPEG. The drug loading efficiency in HSA-mPEG nanospheres by both method was much lower than that in HSA nanospheres. A higher RB concentration was found when the drug was incorporated by the post-adsorption method. RB release from the albumin nanospheres to pH 7.4 phosphate buffer saline solution at 37°C was very slow and the release was dramatically accelerated in the presence of trypsin. The release pattern of RB from the albumin nanospheres can be assumed as erosion control.

Smart Colloids For Molecular Recognition and Controlled Release

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Highly crosslinked, porous polymers prepared in the presence of a templating molecule that is subsequently removed from the polymer matrix show high rebinding selectivity toward the templating species in subsequent studies. Such imprinted polymers are generally prepared by precipitation polymerization, yielding an intractable cake that requires crushing, sieving and sizing before use.

In this study, two methods for the preparation of monodisperse particles that exhibit similar recognition characteristics have been investigated: (a) the miniemulsion polymerization of a divinylbenzene, and (b) a modified precipitation polymerization.

In a parallel study, the possibility of coating monodisperse oil-in-water emulsion droplets with a polymethacrylic acid shell was investigated. The polymer was chosen to produce a shell which expands or contracts with pH. In this way the diffusion of a solute from the oil core to the continuous phase can be controlled by changes in the pH.

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NEUTRON REFLECTANCE STUDIES OF A NOVEL NON-IONIC SURFACTANT AND MOLECULAR MODELLING OF THE SURFACTANT VESICLES

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In the continued endeavours of our research group to determine the relationship between the molecular structures and aggregate structures of surfactants, neutron specular reflectance experiments have been conducted to study the monolayer formed at an air-liquid interface by a novel synthetic non-ionic surfactant, 1,2-di-O-octadecyl-*rac*-glycero-3-(1-methoxydodeca-oxyethylene) (DODE). The reflectivity data were obtained as a function of surface pressure, and were analysed according to the optical matrix method, using single uniform layer fits. The data obtained using the alkyl chain deuterated DODE dispersed on air-contrast-matched water, showed that as the surface pressure was increased from 11mN/m to 34mN/m, the thickness of the monolayer increased from 20Å to 30Å, and the surfactant area per molecule decreased from 186Å² to 99Å²; the equilibrium area per molecule for the surfactant was calculated as 120Å². Using the same surfactant dispersed on D₂O, the numbers of bound water molecules were found to increase (over the same pressure range) from 1.5 to 3.0 H₂O per oxyethylene unit.

On the basis of these monolayer data, computer graphics models were generated for the 3-dimensional structures of the DODE small unilamellar vesicles. Comparisons were then made between the 3-dimensional structures of these non-ionic vesicles, and those formed by the corresponding glycerophospholipid (DSPC). The results obtained are discussed in relation to the applications of the two types of vesicle as vehicles for drug delivery.

THE MEASUREMENT OF THE VISCOELASTIC PROPERTIES OF
ADSORBED POLYMER LAYERS USING A MODIFIED SURFACE FORCE
APPARATUS.

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Many colloidal dispersions both industrial and model, have an adsorbed polymer layer on the surface of the particles. This polymer layer protects the particles against flocculation. When dealing with non-polymer mediated interactions, the use of equilibrium theories for the purpose of describing the interactions is of great value as both the electronic and ionic distributions can respond sufficiently rapidly to ensure that the forces they experience are equilibrium forces. However, in the case of polymers confined between surfaces, a number of distinct relaxation mechanisms can be taking place simultaneously, each with its own relaxation time. Consequently the interactions between compressed polymer layers are often far from equilibrium.

The basic surface force apparatus (SFA) allows the measurement of equilibrium forces, but as mentioned above these are inadequate in the case of polymer mediated systems. We have designed and built a modified version of the SFA which allows us to measure the dynamic properties of a polymer mediated system by application of an oscillatory motion to the adsorbed polymer layers, and monitoring the response. Preliminary results have been obtained for a high molecular weight PEO/PS system suggesting a transition from a purely elastic system at very low separations (~ 100 nm) to a purely viscous system at large separations ($> 1\mu\text{m}$). The system exhibited viscoelastic properties in between these two extremes in separation.

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ROLE OF NATURAL SURFACTANTS IN POLLUTANT BIODEGRADATION IN BIOFILMS ON RIVER SEDIMENTS

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The solid-liquid interface in freshwater environments is important in influencing the patterns and rates of pollutant biodegradation. Moreover, the interaction of various pollutants with sediments is believed to be affected by the layer of natural organic matter (NOM), such as humic substances, found coating some sediment particles. Hence, a four-way interaction can be established between the sediment surface, bacteria, NOM and pollutants. Studies have been undertaken to determine the interaction between two humic substances and a river sediment freed from organic matter. The effects of these humic substances on pollutant adsorption have been investigated by comparing the sorption interaction of sodium dodecyl sulphate (SDS) with both the organic-free sediment and 'native' sediment (with its organic layer intact). Microbial studies to compare the biodegradation of SDS in the presence of these sediments have shown a link between the sorption and biodegradation of SDS, and the attachment of bacteria to particle surfaces.

Sponsored by the Natural Environmental Research Council, Polaris House,
North Star Avenue, Swindon, SN2 1EU

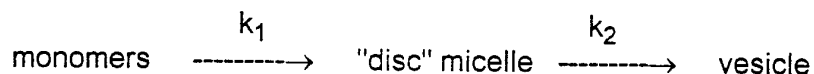
DYNAMIC PROPERTIES OF SODIUM LINEAR ALKYL BENZENE SULFONATE VESICLES.

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Extensive research in vesicles has been reported. However the kinetics and mechanisms of vesicle formation and breakdown are only vaguely understood. In this research, the dynamics of spontaneous vesicle formation *i.e.* assembly of monomers to vesicles, is investigated.

Spontaneous vesicle formation by a synthetic sodium alkylbenzene sulfonate (SLABS) below its critical micelle concentration ($cmc=1.5mM$) is induced by changing the NaCl concentration. A biphasic kinetic rate profile indicates that a two-step process is involved in the formation of vesicles from monomers which possibly involves large "disc" micelles as the intermediates. Approximate rate constant for the formation of 0.5mM SLABS in 30mM NaCl solution were found to be $k_1=0.46sec^{-1}$ and $k_2=0.008sec^{-1}$.



Kinetics studies for vesicle formation and breakdown were carried out using a stopped-flow instrument equipped with uv-visible spectrophotometric detection in turbidity mode. Evidence for vesicle formation is indicated by a polarising microscope fitted with a video recorder.

Studies of the Adsorption and Dissolution of Thin Films using the Quartz Crystal Microbalance

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Thin mixed films based upon the novolak-diazoquinone resin are used extensively in the printing and photoresist industries.

Solubility of the novolak, a cresol polymer, in the developing solution is inhibited by the diazoquinone, the photoactive component. Exposure of the diazoquinone in UV radiation drastically increases solubility of the film, leading to image formation. Obviously as both components are soluble in the developer to some degree, a detailed knowledge of the dissolution process is desirable to both achieve maximum resolution and new film technology.

Research to date has utilised the nanosensitivity of the Quartz Crystal Microbalance to study the dissolution of the novolak component in various cationic and anionic environments. As one might expect a very strong dependance on the cation type and concentration is observed. However, the role of the anion is theoretically less clear with a significant variation observed across a wide range of anions.

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IN VITRO AND IN VIVO CHARACTERISATION OF MODEL POLYSTYRENE NANOSPHERES COATED WITH A SERIES OF SYNTHETIC PEG-PPO-PEG BLOCK COPOLYMERS

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The coating of model polystyrene particles with block copolymers of the poloxamer type has been shown to both extend circulation times *in vivo* and reduce *in vitro* phagocytosis by isolated rat kupffer cells. We have produced a range of synthetic PEG-PPO-PEG block copolymers with a constant PPO segment of mw. 4000 Da and varying PEG chain lengths from mw. 350 to mw. 5000 Da. The *in vitro* kupffer cell uptake and *in vivo* circulation profiles of the copolymers adsorbed onto model polystyrene particles were followed. The *in vitro* kupffer cell assay demonstrated an exponential decrease in uptake with increasing PEG chain length, both in the presence and absence of serum. *In vivo* circulation data also highlighted increased circulation times as the PEG chain length increased. However, only when the PEG chain length of copolymer reached m.w. 1900 Da or over did the particles evade capture by the cells of the reticuloendothelial system. The results compare well to those gained for polystyrene nanospheres coated with commercial Pluronic® block copolymers.

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NEW, IMPROVED, PHARMACEUTICALLY ACCEPTABLE SURFACTANTS

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Surfactants, in particular nonionic surfactants, have for many years been widely utilized as adjuvants in a wide range of pharmaceutical formulations, such as suspensions. More recently the aggregates formed by surfactants upon dispersion in water, for example micelles and cubic phases, have also been investigated as the delivery vehicle *per se*. However in spite of all this interest, the use of surfactants is not as wide spread as might be because of a number of serious limitations that exist with the current range of commercially available surfactants, in particular their high toxicity, low biodegradability and poor drug solubilizing capacity. It is therefore imperative that new, improved, pharmaceutically acceptable surfactants are synthesized.

The aim of the present study is to design, synthesize and characterize micelle forming surfactants with improved solubilising capacity for a wide range of drugs. This goal is being achieved by systematically altering both the nature of the hydrophobic tail chains and the hydrophilic head groups. To date the influence of altering the length of the hydrophobic chain and introducing regions polarity into the core has been established. The results of these studies suggest that it is better to leave the hydrophobic tail region as a straight saturated hydrocarbon chain and alter instead the nature of the hydrophilic head group in an attempt to improve solubilization in this region. Our studies to date support this approach as replacing a polyoxyethylene head group with an amine oxide has been shown to increase, by several times, the solubilization of a wide range of drugs.

It is ultimately hoped that these studies will enable an accurate prediction of the effect of modifying surfactant structure on drug solubilizing capacity.

Industrial (CASE) Sponsor: Glaxo Research and Development, Park Road, Ware, Herts.

PROTEIN-POLYSACCHARIDE INTERACTIONS IN EMULSIONS

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Protein-polysaccharide interactions at the surface of dispersed oil droplets can have a profound influence on their colloidal stability. In this project, the effect of the anionic polysaccharide dextran sulphate on the properties of oil-in-water emulsions stabilized by the proteins bovine serum albumin, β -lactoglobulin or sodium caseinate was investigated. The visco-elastic properties have been studied by small deformation oscillatory rheology and the effect of added polysaccharide on the electrophoretic mobility of the particles analysed by laser Doppler microelectrophoresis. It has been shown that bridging flocculation of the protein-coated droplets by the polysaccharide, as indicated by the electrophoresis findings, leads to an increase in storage modulus of the concentrated emulsions. The flocculation behaviour has been found to be strongest for the sodium caseinate-stabilized emulsions and exhibits a maximum at low polysaccharide concentrations in the case of bovine serum albumin-stabilized emulsions, whereas the effect on β -lactoglobulin-coated particles is less significant. The sensitivity of the bridging flocculation to ionic strength and pH has also been studied.

SURFACTANT STRUCTURE AT ELEVATED TEMPERATURES

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Isabel MacDonald
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Microemulsion systems containing the double-chained, anionic surfactant sodium bis-2-ethylhexylsulfosuccinate (Aerosol-OT, or NaAOT), have been shown to form monodisperse, spherical, water-in-oil microemulsion droplets over a large range of temperature, pressure and composition. Doubly-charged AOT surfactants have been prepared, of the formula $M^{2+}(AOT)_2 \cdot nH_2O$, where $M = Ca, Cu, Ni$ and Zn , in order to determine their properties at elevated temperatures.

Viscosity measurements over the temperature range 25°C - 75°C have been made on solutions of doubly-charged AOT surfactants in cyclohexane, with varying amounts of added water (w). It has been found that with no water added to the system, all of the surfactants have viscometric behaviour which is characteristic of spheres, but at higher w values the viscosities of the systems are seen to increase, which is behaviour more typical of rod-like micelles. This viscosity increase at high w values is lost as the temperature is raised, and is thought to be either due to rod breakdown, or a reduction in rod length.

Electrical birefringence and neutron scattering techniques have been used to find the dimensions of the rods, and to follow the structural changes and changes in dynamic properties as the temperature increases.

Industrial Sponsor;
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SURFACTANT AND GELATIN INTERACTIONS IN AQUEOUS MESOPHASES

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ABSTRACT:

To date, few studies have been reported on the interactions of any water-soluble polymers with surfactant lyotropic mesophases. Gelatin and surfactant interactions have only recently become the focus for detailed experimental studies.

In the present study, the interaction between the amphoteric polyelectrolytes, gelatin (both alkali- and acid- processed), and the aqueous mesophases (e.g. lamellar, hexagonal, cubic, etc.) formed by anionic, cationic, nonionic and zwitterionic surfactant have been investigated. Preliminary results, based on polarised-light optical microscopy, differential scanning calorimetry (DSC), proton and deuterium NMR spectroscopy and low-angle X-ray diffraction, will be reported.

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IN VITRO CHARACTERISATION OF DRUG LOADED SURFACE MODIFIED POLY(LACTIDE-CO-GLYCOLIDE) NANOSPHERES

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The adsorption of the poly(ethylene oxide)-based copolymers Poloxamine 908 and Poloxamer 407 onto the surface of polystyrene and poly(lactide-co-glycolide) particles is known to reduce their uptake by the reticuloendothelial system and extend their circulation times *in vivo*.

The work presented here is the next step in the development of a long-circulating targeted drug delivery system and involves the incorporation of a model drug Rose Bengal into 150nm size PLGA nanospheres and subsequent surface modification with either Poloxamer 407 or Poloxamine 908.

The surface modification resulted in the formation of an adsorbed layer (approximately 6nm) and consequent reduction in the surface charge.

Drug loading was low which can be mainly attributed to the hydrophilicity of Rose Bengal.

In vitro drug release was rapid in buffer medium ($t_{50\%}$ 10 hours) and further accelerated in the presence of serum ($t_{50\%}$ 30 mins) due to the affinity of Rose Bengal for serum proteins.

NEURAL NETWORK COMPUTER SIMULATION OF AEROSOLS

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An ability to predict the behaviour of an aerosol drug formulation upon generation and after administration to the human airways could offer significant benefits to the design of medical aerosol devices, and also facilitate the optimisation of drug delivery *via* the respiratory tract. Previous approaches to such predictions have used mathematical models or particle dynamics coupled with statistics, yielding predictions which give an essentially *static* picture of the aerosol deposition process. Our own researches in this area have been directed towards simulating aerosol *dynamics*. To this end we have explored the feasibility of using an artificial neural network (ANN) to simulate the flow of medical aerosols in the lung. Using computer-generated aerosol test data, we show that this approach may indeed be useful.

A purpose-designed feed-forward back propagation perceptron ANN has been used to simulate the behaviour of a particle cloud moving through a partially obstructed 2-dimensional 'pipe'. In order to generate the 'experimental data' for the test system, the movements of particle clouds through the pipe were computed iteratively over a series of time steps, the redistribution of particles in any given time step calculated by means of a cellular automaton. The ANN was then trained so that the neuronal connection weights were optimised to map a series of input aerosol patterns (for time steps, t) with the corresponding output patterns (for time steps, $t+1$)

After training, the ANN was presented with various different starting configurations of the particle cloud within the pipe, and the progress of the clouds through the system predicted time step by time step. Given the appropriate choices for the network architecture, the experimental data used to train the network, and the parameters governing the training process, the ANNs were found to perform extremely well in these simulations.

We have thus established the applicability of an ANN as a tool for modelling aerosol flow, and are now proceeding to more elaborate models catering for more complex flow patterns in 3-dimensional systems.

CLAY-WATER SUSPENSIONS AS DRILLING FLUIDS

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Imperial College of Science Technology and Medicine

Among the most important functions of drilling fluids is their ability to suspend the cuttings and weight materials during the drilling operation when circulation of the fluid is stopped, control of the subsurface pressure and the formation of filter cakes on the walls of permeable formations. For this reason, most drilling fluids contain a certain amount of clay (commercial bentonite) which provides the system with thixotropic gelation properties enabling the suspension of cuttings upon static conditions and meeting with the viscosity requirements under dynamic conditions.

Non-ionic high molecular weight polymers are used in addition to clay as viscosifying agents to increase the rheological properties of the system and as filtrate loss reducing agents producing uniform filter cakes. They adsorb strongly onto clay particles and improve the stability of clay suspensions under saline conditions and at high temperatures.

In this present work, the rheological properties of clay suspensions have been carried out using steady-state shear stress and oscillatory measurements. These allow the determination of the respective values of yield stress τ_y and elastic component G' as a function of clay concentration. In addition, the adsorption of a special type of nonionic surfactant onto bentonite has been studied. The surfactant is based on a nonylphenol group with propylene oxide and ethylene oxide chains. Adsorption isotherms have been obtained as a function of the molecular weight of the surfactant and salt (NaCl) present in the system. A rough approximation of the surface area of the clay particles was also determined, by the adsorption of methylene blue from aqueous solution.

INTEVEP S.A., Research and Support Center of Petroleos de Venezuela

THE INFLUENCE OF WALL AND INTER-PARTICLE FRICTION ON THE CHARACTERISTICS OF PRESSED CERAMIC PARTS

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A major problem encountered in the compaction of ceramic powder parts is the creation of non-uniform green densities due to powder-die wall and inter-particle friction effects. High wall friction creates high stress gradients within the powder, and hence density fluctuations occur. When sintered, these compacts show deviations from the mould geometry, and hence the final ceramic parts may not be geometrically scaled replicas of the corresponding greens.

This research is focused upon developing compaction and sintering models which predict the density distribution and shape evolution, *i.e.* the near net shape, of sintered ceramic powder compacts. In order to achieve this, preliminary numerical modelling of alumina powder compaction data using the finite element software "LUSAS" (FEA Ltd., U.K.) has been performed. The variation of the wall and internal friction and cohesion coefficients with the applied load has also been investigated.

Industrial Sponsor: British Nuclear Fuels plc, Springfields Works, Salwick,
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LAMELLAR AGGREGATES IN THE L_2 PHASE OF A NON-IONIC SILICONE SURFACTANT (L77-OH)

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The ternary phase diagram for the surfactant L77-OH, water and cyclohexane shows a narrow L_2 region in the oil-rich corner. At 25°C the maximum water solubilisation, as determined by the water-to-surfactant molar ratio, $\omega_{\max}$, is 22.0. Since this is close to the estimated hydration number of the surfactant hydrophilic EO groups reversed micellar aggregates, rather than water-in-oil microemulsion droplets, are believed to be present. Analysis of SANS profiles from the dilute ($\phi < 0.05$) L_2 phase indicates that discrete lamellar aggregates are present at all ω values. The SANS data have been quantitatively fitted using a disc form-factor $P(Q)$ which determines the bilayer thickness (t) and allows an estimation of the lateral dimension through the disc radius (r). At low water content ($\omega \sim 5.0$), where $\omega = [\text{H}_2\text{O}] / [\text{L77-OH}]$, the value of t suggests that the EO chains are in an interdigitated, tilted or coiled configuration. It was found that t increased with ω until at $\omega_{\max}$ the EO chain is apparently fully extended. The radius also increases with ω from 77Å ($\omega = 3.4$) to larger dimensions ($> 200\text{Å}$).

SOLUBILITY OF TESTOSTERONE PROPIONATE IN OIL-IN-WATER MICROEMULSIONS

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Microemulsions are thermodynamically stable, clear fluid dispersions of oil and water, stabilized by a surfactant, usually in conjunction with a cosurfactant, typically a short or medium chain alcohol. Although microemulsions have recently attracted considerable interest as potential drug delivery systems, the requirement for a cosurfactant limits their widespread use. Some nonionic surfactants may however allow the formation of a microemulsion without the need for a cosurfactant. Such cosurfactant-free systems are advantageous in the development of microemulsions for pharmaceutical purposes.

The present study has examined the ability at 25°C of the nonionic surfactant, dimethyldodecylamine oxide, to produce oil-in-water microemulsions incorporating a range of ethyl esters of fatty acids; namely ethyl butyrate, ethyl caprylate and ethyl oleate. The level of incorporation of a lipophilic steroidal drug, testosterone propionate, into microemulsions containing 2% oil phase at 25°C has been determined.

Single phase non-birefringent, water continuous microemulsions were produced with all the oils. However, as the chain length of the fatty acid moiety increased, there was a decrease in the extent of microemulsion existence. The maximum amount of oil incorporated with ethyl butyrate was about 18%w/w using 20%w/w surfactant, while in contrast, the maximum amount of oil uptake seen with ethyl oleate was 5%w/w using 30%w/w surfactant. Interestingly, while the solubility of the drug in bulk oil was greatest for ethyl butyrate and least for ethyl oleate, the level of incorporation of the drug into the microemulsions was least for those containing ethyl butyrate and greatest in those incorporating ethyl oleate. These results suggest that the smaller oils are incorporated into the microemulsion in such a way as to detrimentally alter the hydrophilic head group region, known to be the major site of drug solubilization in micelles and microemulsions, and as consequence in these case counterbalance any advantageous increase in drug incorporation due to the presence of oil.

Industrial Sponsors: Glaxo Research and Development, Park Road, Ware, Herts.

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Reid P. I., Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, CB3 0EL.

ADSORPTION OF ADDITIVES IN WATER BASED DRILLING MUDS ON CLAY MINERALS

Oligomeric polyols and polyacrylamide polymers are common constituents of water based drilling muds (fluid circulated around the drill bit whilst drilling a bore hole) and as such their interaction with the clay minerals which form the bore hole and hence the cuttings produced is of technological significance.

The adsorption of one particular polyol from distilled water and KCl solution onto a swelling clay mineral (Na exchanged SWy-1 bentonite) has been studied by two distinct methods:

- 1. From aqueous solution onto a fully dispersed clay mineral suspension*
- 2. From aqueous solution onto a self supporting film*

The former being analogous to the clay mineral cuttings the latter being analogous to the wall of the bore hole.

The clay-polymer complexes formed in each case have been analysed using FTIR spectroscopy and XRD techniques.

In all cases polyol adsorption causes dehydration of the bentonite and evidence from both techniques corroborate the idea that the concentration of polymer present in solution governs the packing/layering of the polyol between the bentonite platelets.

There is also evidence that the K^+ cation present in the KCl solutions affects the adsorption considerably.

Polymer mixtures are often encountered in drilling fluids and so to simulate the fluid accurately, polyacrylamide of high molecular weight has also been included in the aqueous polyol solutions and the effect of competitive adsorption studied. It has been found that this high molecular weight polymer reduced the rate at which the polyol dehydrated the bentonite films.

Industrial collaboration: Schlumberger Cambridge Research (address as above)

SYNTHESIS OF POLYPYRROLE PARTICLES USING REACTIVE POLYMERIC STABILISERS

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Polypyrrole dispersions have been prepared using novel reactive random copolymer stabilisers. These stabilisers have been synthesised by free-radical copolymerisation and contain pendant thiophene units which participate in the pyrrole polymerisation. The polymeric stabilisers were characterised by proton NMR spectroscopy and gel permeation chromatography (GPC) to determine their comonomer compositions and molecular weight distributions respectively. The polypyrrole particles were characterised by transmission electron microscopy (TEM), photon correlation spectroscopy, infrared spectroscopy (IR) and elemental microanalyses to determine morphology, size distribution and stabiliser content. Conductivity measurements by the four point probe method gave values on the dried polypyrrole colloids as high as 3.6 S cm^{-1} .

Industrial sponser:- Synthetic Chemicals, Four Ashes, Nr Wolverhampton, West Midlands, England, WV10 78P.

THE SONOCHEMICAL DISSOLUTION OF COLLOIDAL MnO_2

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It is well established that the absorption of ultrasound by water can lead to the formation of hydrogen and hydroxyl radicals. In the presence of certain solutes these primary radicals can be scavenged to produce secondary radicals which in turn can initiate a variety of chemical reactions in solution. We have examined the effects of 20 kHz ultrasound on the dissolution of MnO_2 colloids in the presence of aliphatic alcohols. Our results clearly showed that at low alcohol concentrations ($< 0.1 \text{ M}$), the longer the alkyl chain length of the alcohol, the more effective the dissolution of colloidal MnO_2 . At high alcohol concentrations a point was reached where maximum reduction occurred and further increases in bulk alcohol concentration no longer had any effect on the extent of reaction. Collectively, the above observations can be quantitatively explained in terms of the Gibbs surface excess (Γ_{ROH} / molecules/ cm^2) of the alcohol.

THE PROPERTIES OF TRANSITION METAL SALTS OF AEROSOL-OT

Simon Stebbing, University of Bristol.

The Co^{2+} , Ni^{2+} and Cu^{2+} salts of the surfactant Aerosol-OT were studied.

Neutron scattering data showed that the L_2 phase aggregates phase of $\text{Co}(\text{AOT})_2$ were generally cylindrical in shape. The length of the cylinders increased with w ($=[\text{H}_2\text{O}] / [\text{AOT}^-]$), although their radius did not change.

The U.V. absorption spectra of the metal counterions, in the micellar core, changed with w . These changes were interpreted in terms of a distortion of the counterion complex and polarisation of the water ligands at low w . It was suggested that the complexed water helped stabilise the aggregates at low w (≤ 5).

A model based upon packing constraints within the inverse aggregates suggested that:

- : Cylindrical aggregates form over a limited range of w values, at any aggregation number for ions with any hydration radius.
- : Spherical aggregates form at any w value, over a limited range of aggregation numbers and hydration radii.

SEMIFLUORINATED ALKANES - NOVEL "PRIMITIVE"
SURFACTANTS

B.P. Binks, P.D.I. Fletcher, W.F.C. Sager and R.L. Thompson
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Hydrocarbon and fluorocarbon liquids are generally immiscible. Semifluorinated alkanes (SFAs) have the diblock structure $F(CF_2)_n(CH_2)_mH$ (abbreviated to F_nH_m) necessary to act as surfactants in hydrocarbon and fluorocarbon solvents. We have investigated the dependence of the surfactant properties of these functionally "primitive" (chargeless, non-polar) systems on SFA and solvent structure.

Surface tension [1] and X-ray reflectivity measurements have been used to examine adsorption of SFAs at the alkane - air surface. Adsorption increases with increasing F-chain length of the SFA, increasing solvent chain length, and decreasing temperature. Vapor pressure osmometry and light scattering have been used to observe aggregation phenomena. Linear SFA molecules show no micellisation up to their solubility limit in hydrocarbon solvents. We are currently extending these measurements to include fluorocarbon solvents and branched SFA species.

[1] B.P. Binks, P.D.I. Fletcher, W.F.C. Sager and R.L. Thompson, *Langmuir*, (1995), 11, 977-983.

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TITLE OF POSTER: THE PULSED DROP APPARATUS: A TECHNIQUE TO INVESTIGATE THE DILATIONAL RHEOLOGY OF OIL-SOLUBLE SURFACTANTS AT OIL/WATER INTERFACES.

C.F. THORAVAL, Dr T.H. HARDMAN

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ABSTRACT:

The interfacial rheological behaviour of oil-soluble non-ionic surfactants has been studied.

Dilational viscoelastic studies have been carried out using the Pulsed Drop technique. It is a new method which is based on the expansion of a small water droplet in an oil phase containing a surfactant. The measurement of pressure against time shows that a diffusion relaxation mechanism occurs in the re-establishment of equilibrium after an area perturbation. The surface dilational modulus (ϵ_o) and the characteristic frequency (w_o) of the diffusion mechanism for each system were recorded.

The influences of various parameters were studied:

- 1- the surfactant concentration (above and below the critical micelle concentration)
- 2- the size of the surfactant
- 3- the salt concentration in the aqueous phase
- 4- the oil phase

A pure system has been studied, above and below the critical micelle concentration.

Some industrial systems were also studied.

The focus of this work is to study a new technique and to relate the dilational rheology to emulsion stability.

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LOW-ANGLE X-RAY DIFFRACTION AND DEUTERIUM NMR OF THE COEXISTING GEL (L_β) PHASES OF DIOCTADECYL DIMETHYLAMMONIUM CHLORIDE,

John M Walsh, University of Salford

This presentation is concerned with the formation of lyotropic liquid crystal gel phases by the cationic surfactant dioctadecyl dimethylammonium chloride (DODMAC). Gel phases consist of surfactant layers made up of rotating stiff, alkyl chains which are separated by water layers^{1,2}. There are three types of gel phase: normal bilayers, where the chains are perpendicular to the layers, tilted bilayers and interdigitated monolayers. When heated gel phases usually undergo a phase transition to a lamellar phase, in which the alkyl chains are "molten" and thus mobile.

Low-angle X-ray diffraction (EPSRC, Daresbury) and deuterium NMR has been carried out on surfactant/water mixtures in the concentration range ca. 5-80 wt.%.

Above ca. 45°C a single lamellar (L_α) phase is observed. Below this temperature a gel (L_β) phase is formed although some workers³ believe this to be a hydrated solid. The unit cell spacings indicate that the surfactant is organised in an interdigitated monolayer rather than a bilayer. The gel phase shows discontinuous swelling in water, where two gel phases having different water contents coexist over the concentration range ca. 35-75 wt.%.

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MICROEMULSION FORMULATIONS FOR PULMONARY DRUG DELIVERY

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Microemulsions (ME) are considered to be clear, fluid thermodynamically stable dispersions of oil and water stabilised by a surfactant, sometimes in combination with a cosurfactant. Oil-in-water (o/w) microemulsions have recently attracted considerable interest as potential drug delivery systems due to their simple preparation, clarity, stability and ability to increase the solubility of lipophilic drugs. Unfortunately little is known about the relationship between surfactant structure, aggregate type and toxicity. In this study preliminary data pertaining to the interplay between these factors has been obtained.

Phase diagrams of o/w microemulsions produced from two n-alkyl polyoxyethylene ethers surfactants, and a range of triglyceride oils of differing acyl chain length and either water or phosphate buffered saline (PBS) (pH 7.4) at 25 and 37°C have been established. The area of ME existence was seen to depend upon the surfactant and the chain length of the oil incorporated, with no noticeable difference being noted between either of the aqueous phases used. Although there were slight differences in the area of ME formation seen at the different experimental temperatures, the trends were identical. When polyoxyethylene-10-lauryl ether ($C_{12}E_{10}$) was used as surfactant the area of ME existence increased with a decrease in the size of oil (tributyrin < Miglyol 812 < soybean oil). Surprisingly, this trend was reversed in ME produced using the longer alkyl chain surfactant, polyoxyethylene-10-oleyl ether (Brij 97) or $C_{18.1}E_{10}$. Here the largest triglyceride soybean oil exhibited the largest area of microemulsion existence, and tributyrin the smallest.

These ME formulations have been studied for toxicity to human bronchial epithelial cells using the MTT cytotoxicity test. MTT is a water-soluble tetrazolium salt, producing a yellow solution. This tetrazolium salt is converted in living cells to a purple insoluble formazan, which can be assessed spectrophotometrically. As dead cells, in contrast, can not produce formazan, the production of formazan can be used to determine cell viability. The MTT cytotoxicity test has been used in this study to assess the toxicity to human bronchial cells of the various microemulsion systems produced.

Interactions between organosilicon polymers and inorganic particles

Ian Weatherhead, Dr T. Cosgrove, University of Bristol, School of Chemistry, Cantock's Close, Bristol BS8 1TS

This project concerns the interaction of organosilicon polymers with inorganic fillers which are of importance for the manufacture of composite materials. These interactions are believed to determine the bulk properties of such materials. Initial work will focus upon both physically adsorbed and chemically grafted poly(dimethylsiloxane) (PDMS) on silica particles dispersed in a PDMS melt. The silica used will be commercial fumed silica and 'Stober' particles with different distributions of hindered and unhindered SiOH sites. Rheological measurements can be used to study the bulk physical properties resulting from these interfaces. NMR can be used to study the interactions and dynamics of polymer in the bulk and at the silica surface. The structure of the adsorbed/grafted polymer layers can be studied by small-angle neutron scattering.

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PSYCHO-RHEOLOGY

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Psycho-rheology explores the relationship between rheology and our cognition.

Sensory evaluation of many products is frequently employed in markets such as personal care and food. However, the link between rheology and sensory evaluation of tactile cognition is not well understood.

The aim of this work is to establish the link between skin feel and rheology. Novel polymer systems are being used to explore the total range of sensory experience available.

A sensory panel has generated language to describe the skin-feel attributes perceivable during dabbing and spreading on the forearm. Full rheological characterisation shows how viscosity, modulus of elasticity and relaxation depend on shear rate and frequency. Multivariate analysis indicates how this is linked to the sensory attributes.

² Industrial Sponsor: Unilever Research Port Sunlight Laboratory, Quarry
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The Evolution of Microstructure in Particulate Suspensions

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Abstract

The complex rheological response of particulate suspensions arises largely from the subtle nature of the interparticle interactions and their sensitivity to the spatial distribution of the particles - the suspension microstructure. Imposing strain (e.g. by shearing) perturbs the microstructure and so alters the relationships between the macroscopic rheology and the interparticle forces. This results in the complex rheological behaviour. This study is examining means of sensing the evolving microstructure of model suspensions with a view to correlating this properly with the rheology. In flocculated systems, the complex structure of the flow units - the particle assemblies (clusters) that flow as single entities - can be described quantitatively by fractal geometry. The parameters to be used can be obtained from structure-probing techniques. Measurement (a.c. and d.c.), of the conductivity and dielectric properties of a system of conducting particles in an insulating medium (under quiescent and flow conditions) is being employed as the principal structure-probing technique. There is some theoretical basis for calibrating this electrical probe but further analytical development is necessary. The more established scattering techniques, principally neutron scattering, provide an alternative route to the same structural information under quiescent and flow conditions. Computer simulation of the microstructural evolution is being pursued in parallel with the experimental structure-probing work. Ultimately, we hope to prove first order models to predict this evolution of microstructure and its effect upon the sensed rheological response.

LIPASE KINETICS - THE INFLUENCE OF ZETA POTENTIAL ON ENZYME ACTIVITY

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The rate of absorption of dietary lipids in the mammalian gut plays a key role in the complex relationship between diet and disease. Prior to absorption by the gut membrane ingested lipids must undergo a series of biotransformations to increase their solubility in the aqueous environment of the body. The initial stage is the formation of an emulsion during passage through the stomach and the small intestine. The emulsion interface binds and activates the pancreatic lipase/colipase complex which hydrolyses the triacylglycerides into fatty acids and monoglycerides.

Calcium ions are essential requirement for effective binding and activity of the lipase within the physiological environment. To investigate the mechanism of this requirement we have studied the influence of calcium ions on the activity of lipase using an *in vitro* model of duodenal emulsions. Simultaneously the influence of calcium ions zeta potential of these emulsions has been examined.

SOLID SURFACE ENERGIES

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The wetting, spreading and adhesion of liquids on solid surfaces are subjects of great importance in a number of areas of science and technology and they play vital roles in many industrial products and processes. The forces responsible for the interaction of liquid with solid involve the outermost few atomic layers of the surface of the solid and changes to this surface layer provide considerable control over the strength (energy) of adhesion.

To study these properties it is important to characterise the solid in terms of its surface energy which can be split into components corresponding to different intermolecular forces. A simple but very useful approach is to split the surface energy into contributions from dispersion (van der Waals) and polar forces. Estimates of these components can be made by measuring contact angles for at least two probe liquids of different polarity, making use of the Fowkes equation.

A technique will be described which uses contact angle data for a whole series of different probe liquids and a computer optimization to give the best simultaneous fit to the equation for all the data. The technique will be illustrated with some examples of glass surfaces, both clean and containing a surface layer of adsorbed cationic surfactant.

CASE Award sponsored by

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**ADIPIC ACID: DISRUPTION OF CRYSTAL
GROWTH BY ADDITIVE MOLECULES.**

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The incorporation of decanoic acid molecules into the surface growth sites of adipic acid disturbs crystal packing producing crystals with very unusual morphologies. The lattice may be disrupted to such an extent that twinning is initiated. X - ray diffraction has been used to explore the nature of these crystals and investigate the presence of twinning.

In situ observation of crystal growth in the presence of decanoic acid has shown that the interruption of crystal growth begins on one surface. This surface has been examined using the Cerius² molecular modelling suite and is proposed as the site of incorporation of additive molecules.

THE IMPORTANCE OF SURFACE SCIENCE IN PRESSURE FILTRATION

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Abstract

Use of pressure filtration in the chemical, food, pharmaceutical, brewing and mineral processing industries is widespread. Problems arise when colloidal and near-colloidal suspensions form compressible filter cakes; this potentially leads to low filtration rates.

Many parameters are believed to influence cake compressibility, one of which is the surface charge on the particulate material being filtered. The effect of electrokinetic phenomena on cake filtration has been known since the early 1900's. The ability to quantify this influence in order to consider its effect on filter cake formation and subsequent filter design has so far been elusive.

With the aid of an electrical impedance imaging technique, which allows determination of in-situ solids concentrations in solid-liquid mixtures, the effect of surface charge on the formation of compressible filter cakes has been examined. Results will be presented which illustrate the importance of surface forces, solids concentration, pressure etc. in cake filtration. These data, from an ongoing EPSRC funded project, highlight how improvements to filtration processes can be made.

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A STUDY OF THE ADSORPTION OF ANIONIC POLYSTYRENE LATEX
PARTICLES ONTO A NEGATIVELY CHARGED SURFACE IN THE PRESENCE
OF CATIONIC POLYELECTROLYTE

Prof. B.Vincent, Mr. N.Wright
University of Bristol

Thus far a number of polyvinylpyridine-polystyrene (PVP-PS) block co-polymers have been synthesized by ionic polymerization. These have various quaternised PVP and PS block sizes. It is thought that these polymers will bridge between an anionic polystyrene latex particle and an anionic surface: the PS block interacting with the latex particle; and the quaternised PVP (cationic) block acting as an anchor to the surface.

This bridging phenomenon will be investigated using two experimental methods. The first involves the use of a stagnation point flow cell, constructed by a previous Ph.D. student. The complimentary method involves an adaptation to Atomic Force Microscopy (AFM). In this a latex particle will be attached to the cantilever and the force between the particle and a glass slide measured. Measurements will be made with and without pre-adsorbed polymer, and the effect of the solution conditions will be examined.

PHASE EQUILIBRIA IN AQUEOUS POLYETHYLENE GLYCOL/SALT SYSTEMS

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Aqueous colloidal dispersions which are stabilised by copolymers containing ethylene oxide units can be flocculated by the addition of electrolytes. An understanding of this phenomenon requires a model to explain the specific effects of ions on the ethylene oxide-water interactions. To obtain data relating to these effects we have studied the phase separation behaviour of aqueous polyethylene glycol (PEG) solutions to which salts have been added.

Co-existence curves have been determined by turbidimetric titration for mixtures containing PEG 8000 or PEG 4000 with a number of different salts at temperatures in the range 25° to 70° C. The Setchenow equation has been fitted to the binodals to obtain salting-out coefficients for the electrolytes as a function of temperature. An attempt has been made to correlate the coefficients with properties of the aqueous ions that are related to their hydration structures.

A Rheology Study of PEO Solutions at High Pressure

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S. Zhu, B. Briscoe and P. Luckham

Understanding the relationship between the structure of polymers and their viscosity is of fundamental importance in the study of polymers. The role of changes in temperature, solvent quality, concentration, chain architecture, and molecular weight upon the rheological behaviour of polymer solution has been explored by extensive studies. Much less investigated is the role of pressure changes. Pressure being a basic thermodynamic parameter, one can expect that such studies can give insight into the fundamental interactions controlling solution behaviour.

Aqueous PEO solution has a lower consolute solution temperature (LCST). The effect of pressure on the LCST will be investigated. It is expected that the LCST will be reduced as a consequence of the reduced free volume of the solvent. In this work, the rheological behaviour of PEO solution was studied by using two high pressure viscometers (modified HAAKE Rotovisco RV 100 and Rolling-ball rheometer) at pressure range of 1-1500 bar. The influence of solvent property, polymer property of PEO were also considered at the same time.

MODIFICATION OF THE ATOMIC FORCE MICROSCOPE (AFM) TO
STUDY MOLECULAR RECOGNITION INTERACTIONS.

K.Smith, G.Braithwaite, P.F.Luckham. Imperial College, London.

The AFM may be modified to measure extremely small forces, on the order of tens of pico-Newtons. Forces on this scale occur between biologically active molecules when one molecule specifically 'recognizes' the other, a process known as a 'molecular recognition interaction'.

The ability to obtain accurate values for the magnitude of molecular recognition interactions opens up the possibility of precise investigation into the effects caused by changes in the environment surrounding a particular interacting pair of molecules. The technique therefore has far-reaching implications to studies ranging from drug design to affinity separation technologies.

The ability of the technique to scan sample surfaces adds sample mapping according to a specific molecular species and the possibility of use as a specific molecular probe to the potential applications of the modified AFM.

Sponsored by : DTI

ISIS - A RESOURCE FOR COLLOID AND SURFACE SCIENTISTS

Jeff PENFOLD, Richard HEENAN, Steve KING, John WEBSTER & David BUCKNALL

Large-Scale Structures Group, ISIS Facility

ISIS, operated by the newly-formed *Council for the Central Laboratory of the Research Councils* (CCLRC), is an international multidisciplinary neutron beam research facility based around the world's most powerful spallation source.

The ISIS Large-Scale Structures Group operate three neutron instruments of particular interest to the colloid and surface science communities; a small-angle diffractometer called **LOQ** and two reflectometers, **CRISP** and **SURF**.

LOQ investigates the size and shape of large molecules, small particles or porous materials with dimensions in the range 0.6 - 100 nm. Length scales of upto 400 nm can be probed in highly anisotropic systems; eg, where molecules align under the influence of shear or magnetic fields.

CRISP and **SURF** provide information about the thickness and roughness of interfaces on length scales of approximately 0.5 - 400 nm. **CRISP** is optimised for the study of solid/air, solid/liquid or solid/solid interfaces, whilst **SURF** is optimised for the study of liquid/air or liquid/liquid surfaces.

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