Solid State Molecular Science — Professor John White

Neutron and X-ray scattering methods developed by this research group are used to study the structure and dynamics on the nanometre and picosecond space/time scales. Adsorption, self-assembly at interfaces, polymers, the imitation of biomineralisation phenomena using "template" molecules and, most recently, the structure and denaturation of proteins at interfaces are current areas of interest. The insights gained are used to guide chemical synthesis in making new materials with interesting physicochemical properties. One recent highlight has been the first determination of the thermodynamic parameters for protein denaturation in the 50 Å surface layer of a protein solution. By comparison with denaturation in the bulk, the contribution of the surface forces can be measured quantitatively. Another highlight is the first measurement of the interfacial structure of an emulsion surface by neutron reflectivity and the extension of this program to new surfactant design.

Our collaboration with Orica Ltd and Food Science (Australia) on the structure and stability of emulsions has produced scientifically interesting and practically useful information. We continue to show that structural relationships at the nanoscale have importance for rheological and other properties.

Energy Dispersive X-ray Reflectometry

Reflectometry using X-rays can be used for *in situ* structural analysis during thin-film growth. We are particularly interested in thin films based on oxide networks (TiO_2, ZrO_2 and SiO_2) that could find use in heterogeneous catalysis where high surface area is of the utmost importance. One of the most promising routes to new oxide-based mesostructured materials involves the co-assembly of the oxide precursor with an organic template. Using reflectometry with fast time-resolved energy dispersive X-rays, the interfacial structure of these films can be monitored as they self-assemble at the air/water interface. Surfactants such as cetyltriemethylammonium chloride (CTAC) and sodium dodecyl sulfate (SDS) are used as the organic templates. *(With A Hawley, D King, and A R Rennie [NFL Uppsala Universitet, Sweden], A Gibaud [U the Marne, France])*

Evaporation-induced Self-assembled Thin Films

A collaboration has begun with the University of the Marne (France) and Uppsala University (Sweden) to study evaporation-induced self assembly (EISA). This has been used previously to prepare thin mesostructured silica-based and transition metal oxide-based films including TiO_2 and ZrO_2. Using the micellar template concept followed by calcination, optically uniform mesoporous thin metal oxide films can be realised. *(With A R Rennie [NFL Uppsala Universitet, Sweden], A Gibaud, J-F Bardeau [U the Marne, France])*

Solvent Effects in High Internal Phase Emulsions

Our previous work using small angle neutron scattering (SANS) and neutron and X-ray reflectometry on high internal phase emulsions has concentrated on an archetypal high internal phase emulsions in which surfactant nature, concentration and molecular weight have been varied. We have shown that these consist of polydisperse micron-scale aqueous droplets, 90% by volume, suspended in a continuous 10% by volume hexadecane oil phase. This year we have completed the investigation begun last year of variation in the oil phase by collection of complete sets of SANS data within the

phase space hexadecane-toluene-cyclohexane as a function of temperature, both from emulsions and microemulsions, together with the collection of emulsion rheological data. *(With K J Baranyai, M J Henderson, J Zank, P A Reynolds)*

Ultra Small Angle Scattering from High Internal Phase Emulsions

SANS can only probe scales from *ca.* 1 to 50 nm in high internal phase emulsions, while optical methods probe scales greater than *ca.* 1000 nm. Coverage of this gap between SANS and optical microscopy potentially provides a complete structural description. We have continued and completed experiments detailed in the 2003 Report by further use of the USANS instrument BT-5 at NIST to provide data from 20000 nm down to 60 nm on high internal phase emulsions with various neutron contrasts. *(With K J Baranyai, P A Reynolds, M J Henderson, A J Jackson, J Zank, and J Barker [NIST])*

The Synthesis of New Surfactants

A range of new surfactants have been synthesized to investigate the factors influencing the stability of high internal phase emulsions formed with them at lower surfactant concentrations. They are block oligomers formed from a large variety of monomers with modified headgroups. This new synthetic ability has also allowed us to synthesise partially deuterated surfactants for use in investigations of mixed surfactant emulsions. *(With J Zank, A J Scott)*

Proteins at Surfaces

The effect of interfaces on the thermodynamics and kinetics of protein unfolding is accessible by reflectometry using X-rays and neutrons at interfaces. Present work is directed at following the changes in surface excess of a globular protein adsorbed at the air-water interface in the presence of a chemical denaturant. The experiments probe the equilibrium surface structure of bovine β-lactoglobulin solutions containing increasing concentrations of guanidinium hydrochloride (G•HCl) at constant temperature. A measure has been made of the contribution of the air-water interface to the chemical denaturation enthalpy of β-lactoglobulin. *(With A Perriman)*

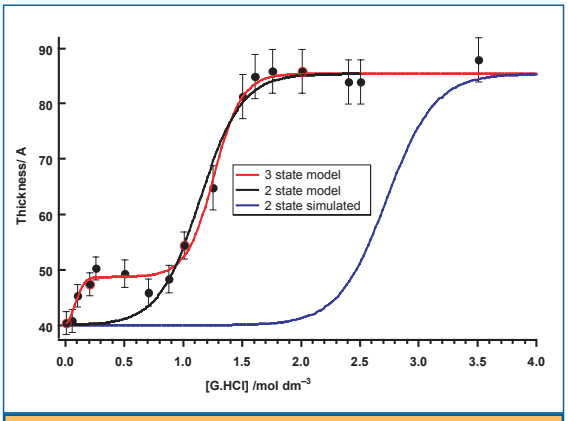

Figure: Thickness parameter as a function of chemical denaturant concentration for β-lactoglobulin at the air-water interface. Solid lines result from application of a 2-state (black), 3-state (red), and solution thermodynamic parameters (blue).

Denaturation of Proteins at Interfaces at the Nanometre Scale

Dried dairy ingredients are an important segment of the Australian dairy market. In the case of high protein content powders a loss of functionality (*e.g.* solubility) is observed on drying. Our aim is to understand the nanoscale structural changes that occur on dehydration and the factors influencing those changes. *(With A J Jackson, and M A Augustin [Food Science Australia])*

http://rsc.anu.edu.au/research/white.php