



SOLID STATE MOLECULAR SCIENCE

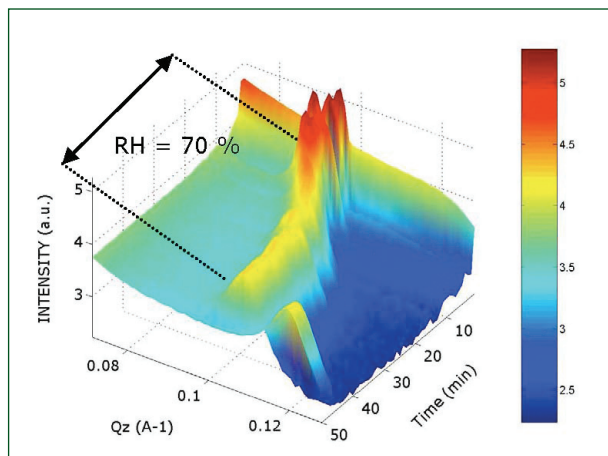
PROFESSOR JOHN WHITE

Neutron and X-ray scattering methods, developed by this research group, are used to study the structure and dynamics on 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 useful practical information. We continue to show that structural relationships at the nanoscale have importance for rheological and other properties.

Titanium Oxide Films for Solar Energy Capture

Titanium dioxide is an inexpensive and stable semiconductor material. Its wide bandgap, however, (ca. 3.2 eV) allows



Time resolved X-ray reflectivity of a growing titanium oxide film showing quick de-swelling at (ca. 40 minutes) when humidity was changed from 70% RH to 30% RH.

for the capture of only 2–8% of the solar photon flux. A shift in the optical response of TiO_2 from the UV to the visible spectral range will increase the effect on the photocatalytic efficiency of the material. Our work concerns the preparation of thin mesoporous TiO_2 films (800 – 3000 Å) doped to provide a shift in the optical response. The films have been prepared by a surfactant template route using evaporative induced self-assembly (EISA). During the year the collaboration identified the conditions required to form well structured films reproducibly; characterised the film structure at each step of the process with reflectometry using X-rays and neutrons; nitrogen doped the oxide framework; and removed the surfactant template with an ethanol rinsing treatment prior to calcination at 400 °C to help prevent collapse of the oxide structure. (With M J Henderson, and A Gibaud [Laboratoire de Physique de l'Etat Condense, Le Mans, France], A R Rennie [Uppsala U, Sweden])

Solvent Effects in High Internal Phase Emulsions (SANS and USANS Analysis)

Previous work using small angle neutron scattering (SANS) and ultra small angle neutron scattering (USANS) focused on high internal phase emulsions (90% aqueous phase/10% oil phase) in which surfactant nature, concentration and molecular weight have been varied. This year we have completed a comprehensive study on the effects of variation in the oil phase on the emulsion structure. The oil-phase consisted of mixtures of hexadecane and toluene in different ratios. The research

has been supplemented by small angle X-ray scattering data and viscometry on surfactant solutions in the corresponding hexadecane/toluene mixtures. The combination of USANS, SANS (various neutron contrasts) and optical microscopy enabled us to develop a complete structural description of the emulsion system. The polyisobutylene-based surfactant stabilises the droplets within the emulsion by monolayer formation at the aqueous/oil interface, and by formation of nanometer-scale reverse micelles within the oil phase. The obtained data have been fitted to a model of linked micron scale surfactant-rich blocks, whose number, size and dimensionality of linkages vary systematically with the surfactant-oil interaction. The model results reveal that the compatibility of surfactant with oil is the major factor in the type, size and relative amounts of observed emulsion structures. *(With K Baranyai, A J Jackson, P A Reynolds, A J Scott, J Zank, and J Barker [NIST, Gaithersburg, USA])*

Synthesis and Characterisation of Novel Surfactants

A plethora of novel surfactants for a potential application in high internal phase emulsion systems have been synthesised. Access to a large variety of monomers enabled us to prepare block oligomers with defined properties. The compounds have been characterised by Gel Permeation Chromatography (GPC) and Modulated Differential Scanning Calorimetry (MDSC). In order to understand and predict the behaviour of the surfactant molecules at the water-oil interface, the behavior at the water-air interface (Langmuir Trough) served as a model. The aim of our work is to investigate the stabilisation mechanism of these amphiphiles when used at lower concentration, for the preparation of high internal phase emulsions. *(With J Zank, A J Scott)*

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. We are employing scattering techniques (neutron and X-ray) to examine the nanoscale structural changes that occur on dehydration. Our aim is to relate these changes to the observed loss of functionality and propose methods to restore that functionality. *(With A J Jackson, and M A Augustin [Food Science Australia])*

Kinetics of Adsorption of Lysozyme at the Air/water Interface

The adsorption kinetics of Hen Egg White Lysozyme at the air/water interface has been studied using specular neutron reflectometry. Experiments were performed at a number of pH values to examine the effect of charge on the rate of protein adsorption. Solutions of Hen Egg White Lysozyme in Air Contrast Matched Water at 1 mg/mL were made. These allow direct determination of the surface excess of protein. High repetition experiments with short collection times were used to accurately determine only the surface excess, derived from the product of the film thickness and the scattering length density of the layer. The kinetic traces at pH values where the protein is charged, are well fitted by a first order rate equation with two linear regions, where the change in the gradient occurs as the surface concentration reaches a steady state. This behaviour is characteristic of the transport and distortion of protein molecules, followed by rearrangement in the surface layer. The equilibrium concentration is a function of protein charge with steady state surface concentrations reaching 1.4 mg m⁻² at pH 4 and 3 mg m⁻² at pH 11. Protein charge is inversely related to the rate of adsorption. This dependency has been explored through use of thermodynamic analysis. *(With A W Perriman)*

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