

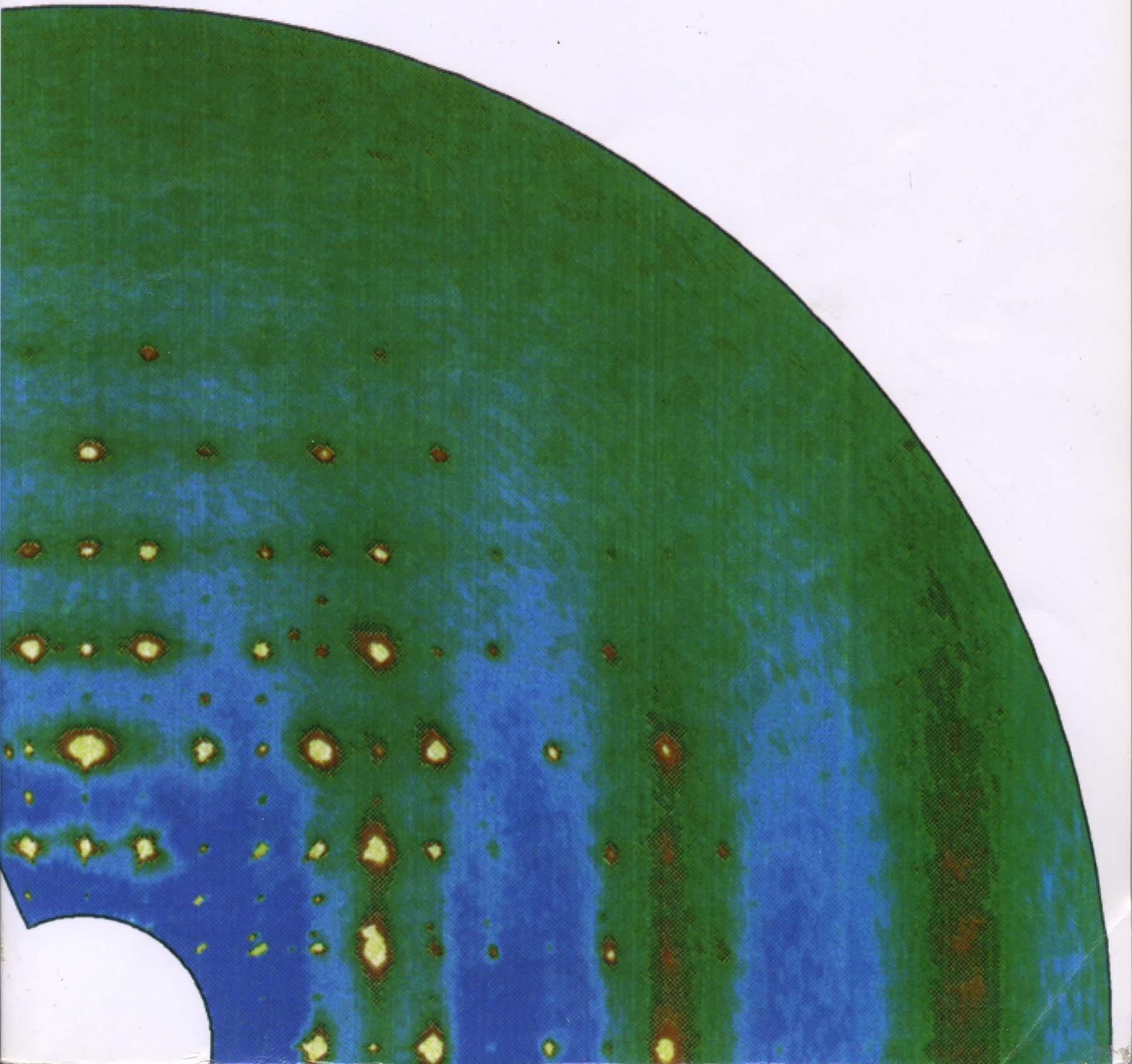


CLRC

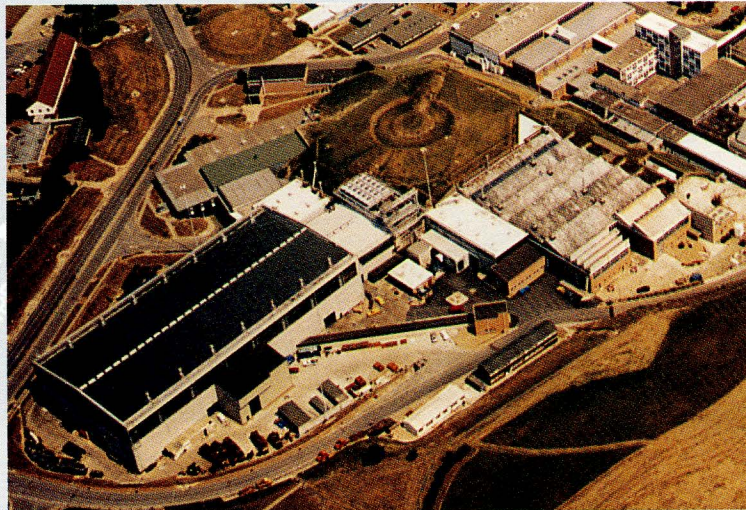
COUNCIL FOR THE CENTRAL LABORATORY
OF THE RESEARCH COUNCILS

ISIS 96

The ISIS Facility
Annual Report 1995-96



FOREWORD



It has been an excellent year at ISIS both from the point of view of the performance of the source and the quality of the science. The intensity and reliability of the source improved throughout the year, culminating in the final cycles where the magic figure of 200 μA consistently appeared on the display in the hall. Indeed daily averages in excess of 200 μA in December demanded a champagne celebration! This superb performance resulted from a better understanding of the dynamics of the machine and the implementation of feedback controls on the ion source and the synchrotron, as well as the hard work and dedication of those operating the accelerator and target systems.

There was another champagne celebration — this time courtesy of His Excellency the Australian High Commissioner — on the occasion of the inauguration of SURF by Sir John Cadogan. Further instrument upgrades are in the pipeline thanks to the same CRG mechanism which delivered SURF: a dedicated high pressure diffraction station has been built on PEARL (Pressure and Engineering Research Line), the former test beam; the IRIS guide has bifurcated in readiness for the construction of the polarisation analysis spectrometer, OSIRIS; even in its design phase, the MAPS project has already had a major impact on single crystal excitation studies at ISIS through advances in analysis and visualisation software; and there is great anticipation in the diffraction community about the prospects of GEM. Tensioning instrument development against grants has clearly worked!

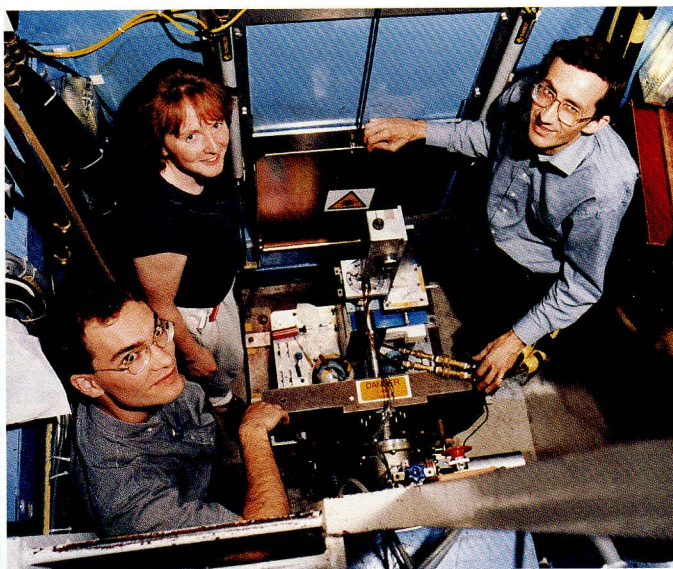
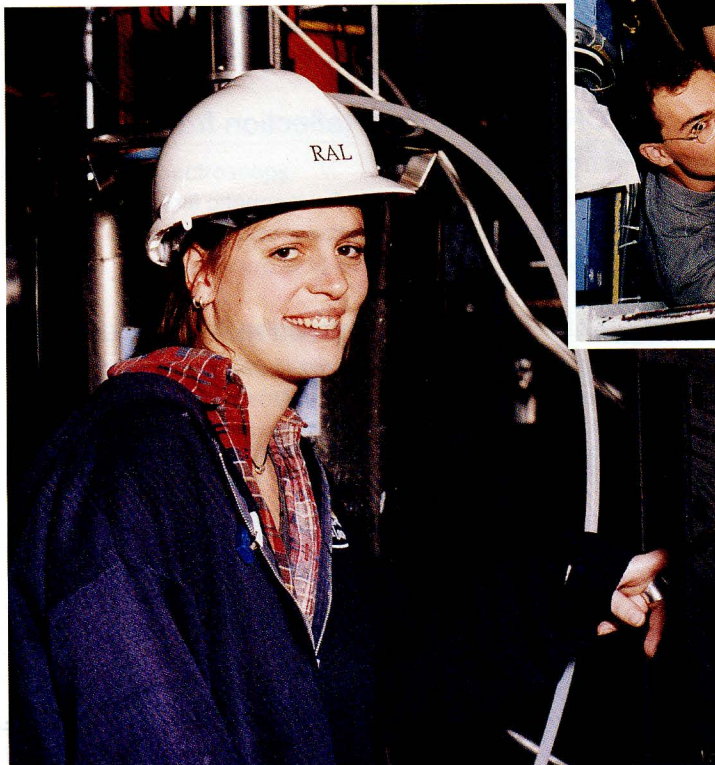
Neutrinos and muons at ISIS are also flourishing. A major activity has been the upgrading of the KARMEN experiment by constructing a massive active scintillator shield within the 8000 tonne passive steel shielding, and there has been a wonderfully successful start to the μCF programme on the RIKEN facility.

Foresight is a terrible thing. Last year's foreword to ISIS 95 highlighted the need for a concerted dipole magnet refurbishment programme, but, given the funding situation, the decision was to operate today and to delay maintenance until tomorrow. During the recent run-up after the winter shutdown, damage to an rf screen in one of the main dipoles reduced the beam aperture limiting ISIS to 135 μA — still the world's most powerful facility, but well below our potential. Insufficient finance in previous years has meant that no spares are available and we will have to wait till the autumn to effect a repair.

An advantage of the new funding arrangements soon to be introduced by EPSRC is that UK users will generate income directly related to the quality of their scientific programmes at ISIS: we will no longer be capped at an arbitrary funding level and will get the support we deserve!

Alan Taylor

Below: Tessa Brennan (Bath University) operates the cryomagnet during investigation of Tb phosphate glasses on POLARIS. [96RC1356]

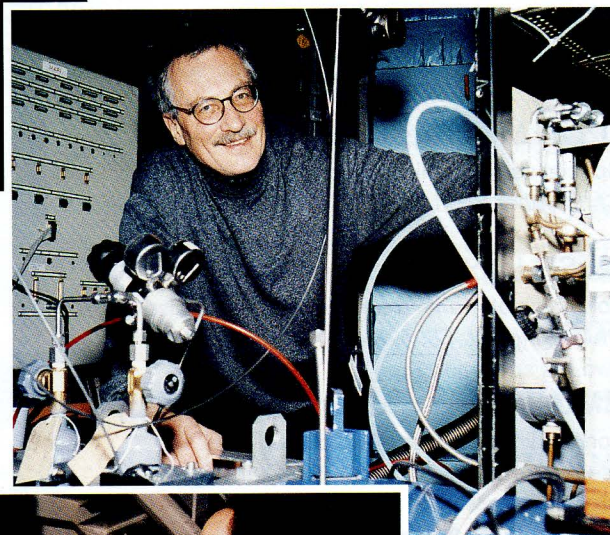


Above: Anne Young and C. Brigault (Brunel University) using the LOQ shear cell with Richard Heenan. [96RC3719]

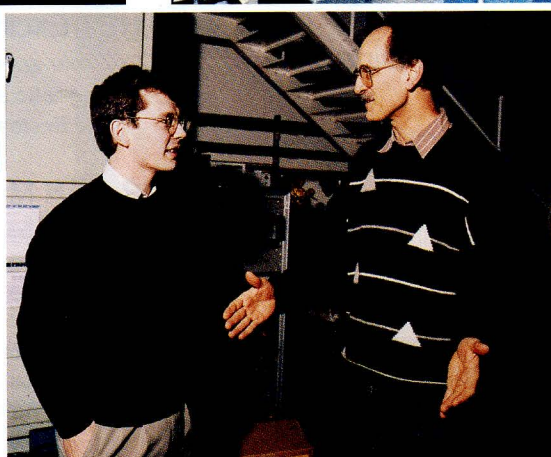
Below: Kurt Guckelsberger (Braunschweig) studies He on MARI. [96RC1064].



Above: Richard Todd (UMIST) mounts his ceramic composite sample in order to measure residual stress on HRPD. [96RC1260]



Right: Stephen Blundell (Oxford University) and Dierk Herlach (PSI) talk about muons. [96RC1257]



LARGE SCALE STRUCTURES

Neutron reflectometry and small angle neutron scattering, SANS, are key techniques in the study of soft matter, complex fluids, surfaces and interfaces. On the small angle diffractometer, LOQ, and on the reflectometers, CRISP and SURF, there is a vigorous and extensive experimental programme in these fields, which exploits the features of pulsed neutron sources: a wide dynamic range and the capability of good resolution.

CRISP / SURF

In neutron reflectivity (on both CRISP and SURF) there is a clear trend towards the study of complex systems and environments, and more detailed structural features.

The detailed structural studies have involved measurements of alkyl chain conformations (with partial labelling of groups of two or four methylenes) of cationic and non-ionic surfactants (Thomas, **A283**) extending the initial work reported in *ISIS 95*, of the structure of catanionic monolayers (Eastoe, **A257**), of di-chain non-ionic surfactants (Barlow, **A254**), surfactant mixtures (Penfold, **A268**, **A292**), polymer

mixtures (Richards, **A447**) and surfactant /alkane mixtures (Fletcher, **A269**).

Interesting conformational changes in sugar based non-ionic surfactants adsorbed at the air-water interface have been demonstrated (Thomas, **A283**). Sugar based non-ionic surfactants have aroused much recent interest because of environmental issues (they can be synthesised from renewable resources). The monolayer is smooth in comparison to what is found for other systems, and its roughness at the cmc (critical micellar concentration) can be entirely accounted for by capillary waves. At the cmc the molecule as a whole appears to be tilted by 35-40° away from the surface normal, whereas at cmc/400 the chains are approximately normal to the surface, while the glucanamide groups are strongly tilted (figure 2.7).

Work on the location of counterions in a surfactant monolayer (Bain, **A253**) illustrates well the fine structural detail that is accessible with judicious isotopic labelling. The alkyl trimethyl ammonium bromide (C_n TAB) surfactants in the presence of certain counterions (tosylate, benzoate, and salicylate) transform from spherical micelles to wormlike aggregates with highly non-Newtonian viscoelastic properties. The origins of these transformations and the nature of the binding of such counterions is not well

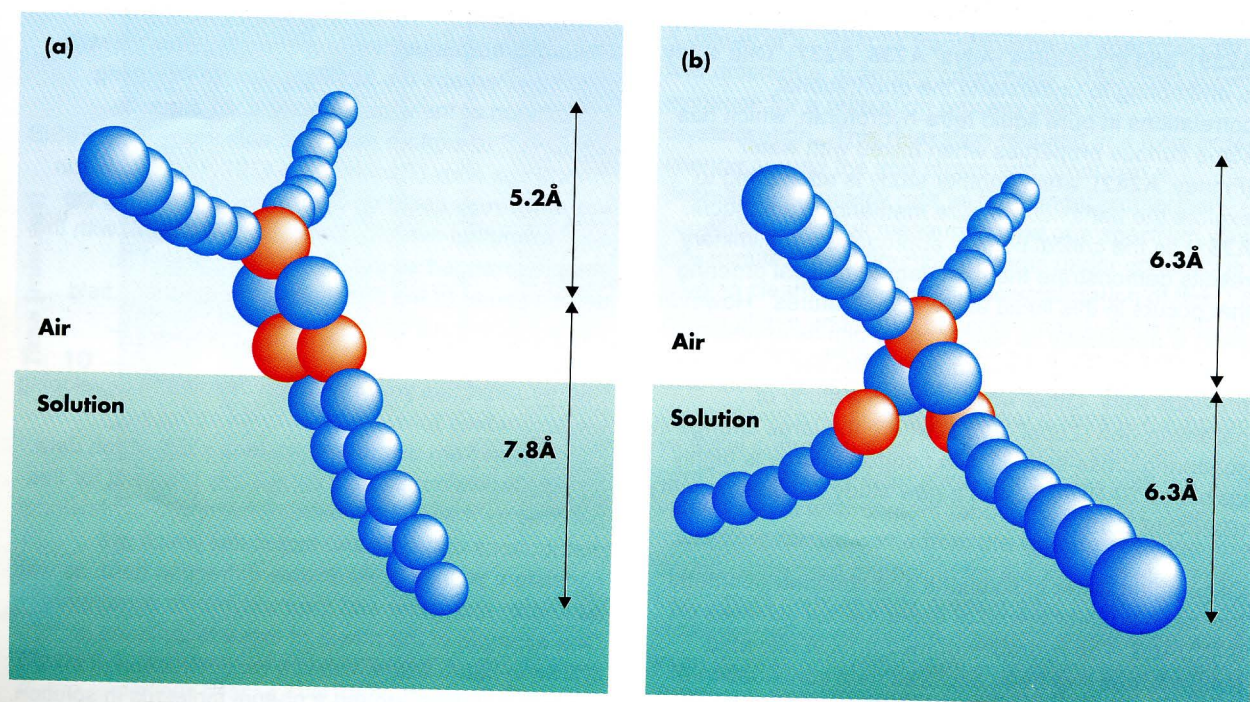


Figure 2.7. Schematic representation of the adsorbed 7,7-bis [1,2,3,4,5-pentahydroxy hexanamidomethyl]-n-tridecane surfactant at the cmc and cmc/400.

Diffraction studies of vermiculite clay hydration: the structure of solid-solution interfaces

N T Skipper, G D Williams, M V Smalley (University College London), A K Soper, S M King (ISIS)

A detailed knowledge of the structure developed at solid-solution interfaces is essential if we are to understand many important natural and industrial processes. These include colloidal interactions, electrode reactions, crystal growth and dissolution, oil and gas migration, polypeptide folding, and membrane formation and stability. Unfortunately, in most real systems the surface area presented to the liquid is poorly oriented and/or relatively small. This makes high resolution diffraction studies of the interfacial region very difficult. Vermiculite clay minerals are a notable exception. These materials contain extremely large and well-aligned internal surface areas, and readily absorb a variety of interesting guest molecules, including water and alcohols. Time-of-flight neutron diffraction studies of such vermiculite crystals, used in conjunction with isotopic labelling of the adsorbed interlayer species, provide a very detailed picture of the liquid phase structure close to the clay surface.

Vermiculite Clay Swelling

Vermiculites are expanding clay minerals that occur naturally as macroscopic (cm^3) crystals. They are widespread in soils and sedimentary rocks, and have a large number of practical applications. For example, they are used in drilling fluids, catalysts, landfill site liners and soil conditioners. Vermiculite crystals comprise stacks of negatively charged mica-like sheets which are held together by charge-balancing interlayer counterions, such as lithium or calcium. In the presence of water and other polar solvents these interlayer counterions have a strong tendency to solvate, thereby forcing the clay layers apart in a series of steps. This process is known as crystalline swelling and produces samples with clay layer spacings of up to about 20 Å. Under certain conditions, and with certain interlayer counterions, crystalline swelling of vermiculites is followed by the uptake of additional solvent, causing macroscopic swelling. This macroscopic swelling results in the formation of colloidal gels that are characterised by a regular, controllable, clay layer spacing of up to about 1000 Å.

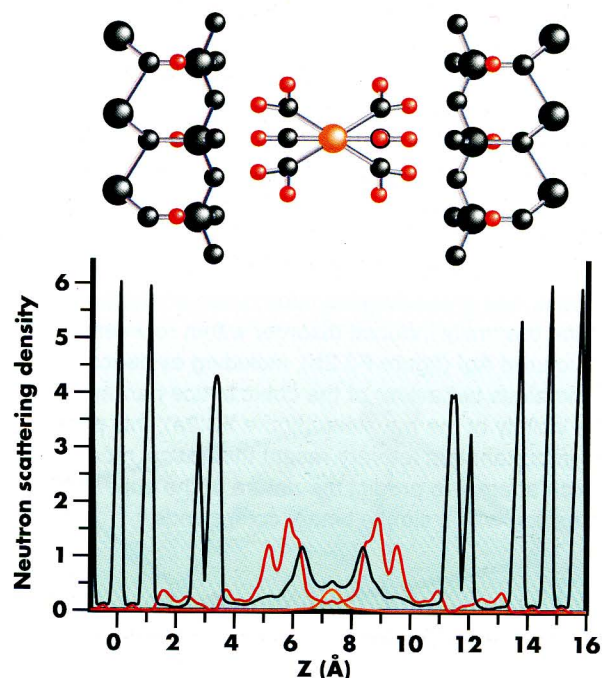


Figure F4.1 Interlayer structure in hydrated lithium vermiculite. The scattering density profiles show that each lithium ion is hydrated by six water molecules. Three profiles are shown: black – unsubstituted species; red – hydrogen; orange – lithium.

Neutron diffraction is proving decisive in resolving the interlayer structure and swelling behaviour of vermiculite clays. Isotopic substitution, for example deuterium/hydrogen, can be used in conjunction with difference analysis to label and locate individual interlayer species. The large Q-range accessible through instruments such as LAD and LOQ provides unrivalled real-space resolution for both crystalline and colloidal systems. Vermiculite crystals can be aligned so that structure parallel and perpendicular to the clay layers is measured simultaneously by different detector banks, without the need for sample rotation.

Earlier neutron diffraction studies of crystalline vermiculites containing simple mono- and divalent counterions showed that the interlayer region is highly structured, with very strong hydrogen bonding of adsorbed water molecules to the clay surfaces. In addition, isotope substitution of interlayer $^6\text{Li}^+$ for $^7\text{Li}^+$ has enabled us to measure for the first time the counterion density as a function of distance from the clay surfaces in the so-called electric double layer. This density profile, figure F4.1, shows that counterion solvation is a precursor to colloidal expansion.

Inelastic neutron scattering studies of alginates for wound dressing applications

C Sartori, D S Finch, B Ralph (Brunel University), K Gilding (Innovative Technologies), S F Parker (ISIS)

Alginates are hydrophilic polysaccharides found in brown seaweeds, comprising up to 40 wt% of the dry matter. Sodium alginates are well known for their ability to form a gel in contact with most divalent cations, and this property has been widely used in the food and drinks industry, as well as in the pharmaceutical sector. On contact with blood, a calcium alginate will rapidly release Ca^{2+} ions in exchange for Na^+ ions, stimulating blood coagulation and making it an ideal choice for wound dressing applications. In order to extract information on the location of the ions within the alginate molecules, both infrared and Raman spectroscopies have already been used. However, the formation of a gel network is believed to involve mainly intermolecular links such as hydrogen bonding. Neutron spectroscopy is perfectly suited to the study of such types of bonding and complements the two previously mentioned techniques. Inelastic Neutron Scattering (INS) studies of alginates have been performed on the TFXA spectrometer at ISIS.

The main function of alginates in seaweed is skeletal, giving both strength and flexibility to the algal tissue. Alginates contain β -D-mannuronate (M) and α -L-guluronate (G) blocks, linked randomly by $-\beta$ 1,4 and $-\alpha$ 1,4 glycosidic bonds; the molecular structure of sodium alginate is shown in figure F9.1. The sodium ion is understood to be bound to the carboxylic groups

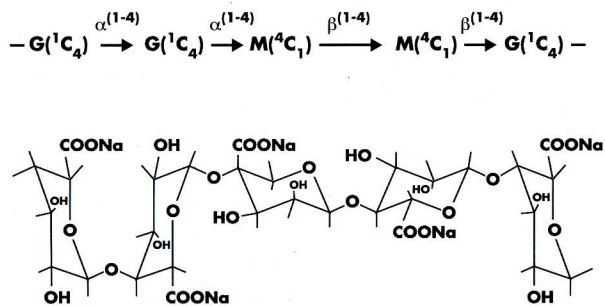


Figure F9.1 The structure of sodium alginate.

COO^- of the alginate molecules. In calcium alginate, the “egg-box model” has been developed to explain the location of the Ca^{2+} ions, predominantly within the G-block (figure F9.2). This is based on the fact that G-blocks are more easily able to chelate the calcium ions, because a spatial arrangement between adjacent blocks forms a “box” in which the ion can reside. However, this model does not seem to apply to other divalent cations (Cu^{2+} , Co^{2+} , Mn^{2+}) and therefore its validity needs to be verified.

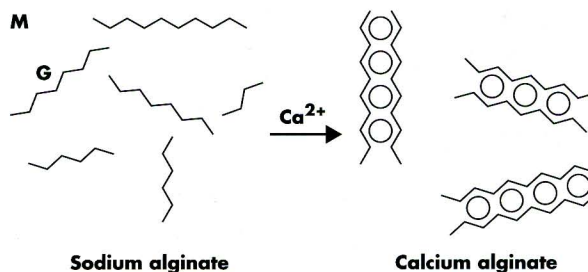


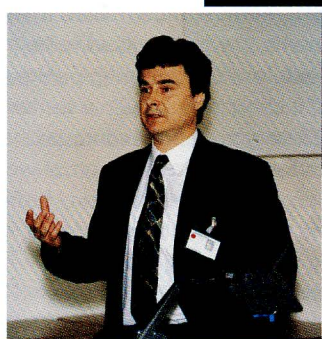
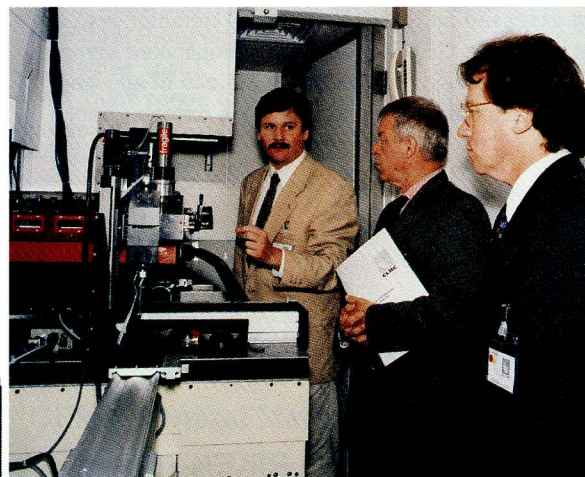
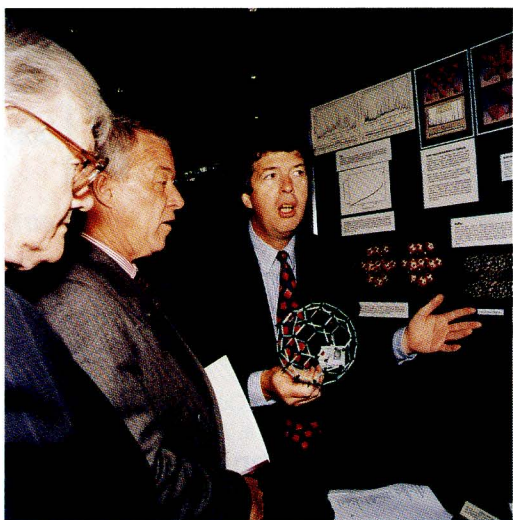
Figure F9.2 Location of Ca^{2+} in calcium alginate.

Different alginate films were prepared, as salts of Na^+ , Ca^{2+} , Zn^{2+} (due to its higher covalent character with C and O) and Ag^+ (silver, although a monovalent ion, has been proved to induce gelation in alginates). For each salt, two different alginates were used (both provided by Pronova Biopolymers Ltd. of Norway) with different M and G contents: a high-G alginate with $\text{M/G} = 32/68$, and a medium-G alginate with $\text{M/G} = 52/48$.

INS spectra of these samples were recorded for approximately 12 hours on TFXA. Modes that involve significant hydrogen displacement dominate the spectra (due to the high scattering cross-section of hydrogen).

The spectra obtained for the high-G alginate are shown in figure F9.3 from 0 to 2000 cm^{-1} . The broad peak at $\sim 600 \text{ cm}^{-1}$ is representative of water molecules (librational mode of vibration). By calculating the ratio against the highest peak at 1350 cm^{-1} , it appears less dominant for silver and zinc than for the two other salts. This correlates with previous thermogravimetric analysis carried out on the same samples: the water

The SURF Inauguration



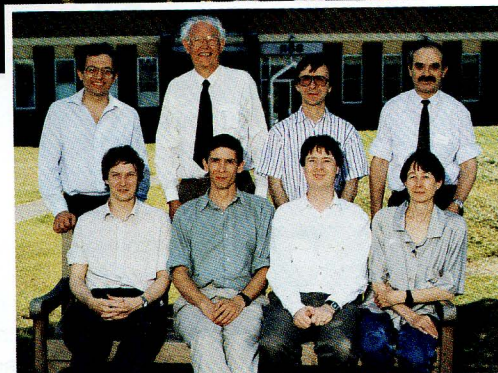
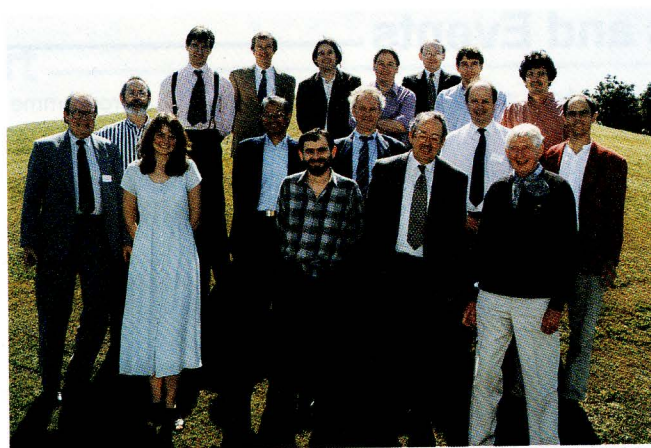
The SURF plaque unveiled by Sir John Cadogan, Director General of the Research Councils (centre left), in the presence of Dr Andrew Taylor, Head of ISIS (left), his Excellency the Honourable Dr Neal Blewett, Australian High Commissioner (centre right), and Dr Paul Williams CBE, Chairman and Chief Executive of the CCLRC. [96RC3742]

Top left: Dr Andrew Taylor explaining the principles of neutron scattering to Dr Blewett and Sir John Cadogan. [96RC3737]

Top right: Dr John Webster shows the Australian High Commissioner the latest addition to the ISIS instrument suite. [96RC3736]

Left: Dr Rob Richardson of Bristol University (top) and Dr Ed Staples of Unilever during lectures on the scientific potential of SURF. [96RC3725], [96RC3729]

IBM Panels Round 2/96



Top: IBM-1, Crystallography [96RC3238]. 2nd row, left: IBM-2, Liquids and Amorphous Materials [96RC3260]. 2nd row, right: IBM-3, Large Scale Structures [96RC3239]. 3rd row: IBM-4, Excitations [96RC3244]. 4th row: IBM-5, High Resolution Spectroscopy [96RC3241]. Bottom: IBM-6, Muons [96RC3237].

