



14. Neutron Scattering in Soft Matter Physics and Chemistry

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Abstract

Recent experiments area of soft matter science show that self assembly on the micron scale as well as the nanometre scale can be directed chemically[1].

This lecture illustrates how such processes can be studied using the contrast variation available in neutron scattering through isotopic replacement and the techniques of neutron small angle scattering and neutron reflectivity. Related dynamical information at nanometre resolution and on time scales between a nanosecond and a few tenths of a picosecond will become accessible with brighter neutron sources.

The examples presented concern the template induced crystallisation of zeolites, the liquid crystal template induced synthesis of mesoporous materials and the structure of thin films at the air water interface .

1. Introduction

Neutron scattering is proving to be a most valuable method for determining structure on the nanometre distance scale and the nanosecond to picosecond time scale. The scope of these methods for physics, chemistry, biology and industry has been reviewed by the European Science Foundation, the "Autrans Report"[2]. A key area is that of "soft matter" chemical physics, which encompasses the structure and dynamics of surfactant films and solutions, of polymeric solids and fluids, colloids, emulsions, liquid crystals and gels. These are fields of considerable industrial importance previously thought to be intractable. A

comprehensive account of recent advances in one "soft matter" area, thin film structure has recently appeared [3].

2. Imitating the processes of Biology for New Materials Synthesis.

Functional structures of biological systems are produced by intermolecular forces mediated by temperature and the chemical composition of the assembling components. The same forces give rise to conformational and demixing phenomena in polymers and polymer blends, in glasses, ceramics and colloidal aggregates. Neutron scattering methods, both elastic and inelastic are key methods for determining the structure and dynamics of such systems and in that work the phenomenon of isotopic contrast variation (eg by selectively deuterating components of the system, is of unique value. In chemistry, a major program in Australia is to use neutron scattering methods to examine the role of molecular templates, liquid crystal templates, and molecular films under imposed stress in changing the self assembly process. The objective is to control the synthesis of new materials based on self assembly. We use this example to illustrate some of the power of contrast variation in small angle scattering and reflectometry.

3. Molecular Templates and Zeolite Synthesis

Lok *et al* [4] identified zeolite crystallisation as one of the most complex chemical problems of the time. They not only commented on the role of gel chemistry, but also on the role of the template cations used in the synthesis. It has been the goal of our work for some time to identify the first steps in the template induced structuring process using scattering methods. An understanding of such template directed self assembly, and of the nucleation and growth mechanism are central themes in the design and synthesis of new and useful zeolitic materials, the most widely used catalysts in the petroleum industry. Previously we have shown by small angle neutron scattering that in a gel based silicalite synthesis mixture a very high degree of template incorporation into the gel occurred at room temperature soon after the mixing of components. We have now found a system for which *homogenous* nucleation of silicalite occurs, and this greatly simplifies the interpretation.

In situ small angle x-ray (SAXS) and neutron scattering (SANS) from this system has been followed as a function of time when heating at 100°C[5,6]. The radius of gyration and intensity of scattering grew from 22 Å at 30 minutes until there was a maximum "size" and particle density at the 14 hour mark. Thence, there is a continual decrease in the number of particles over the next 18 hours with no larger particles being detected by the SAXS machine.

These results are consistent with the hypothesis that particles grow to a size of $R_g = 81 \pm 5 \text{ \AA}$ and then rapidly aggregate into larger secondary particles. SANS showed similar trends, but allows contrast to be varied so as to identify the presence of the tetrapropylammonium (TPA) template in these tiny colloidal particles.

In this study the scattering length density of the solvent was varied by changing the D_2O/H_2O ratio in the solution. Also, by using both hydrogenated (h28-TPA) and deuterated (d28-TPA) template, the scattering length density of the nuclei was varied.

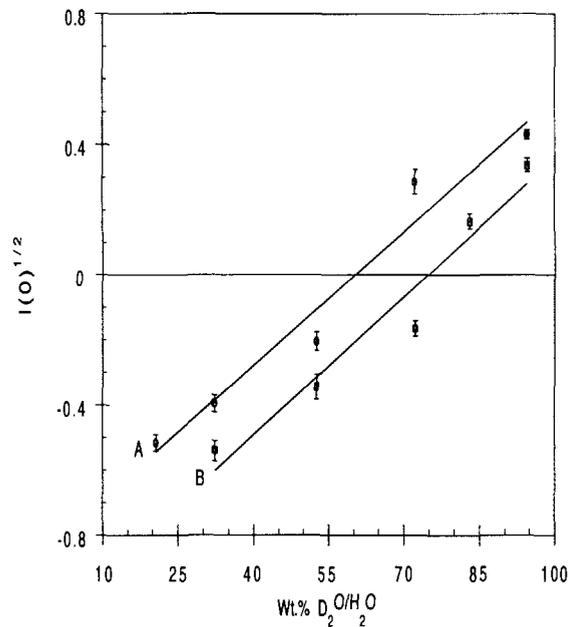


Figure 1 Contrast variation plots of the SANS intensities for silicalite solutions heated for 5 hours with A) h28-TPA template and B) d28-TPA template.

For h28-TPA and d28-TPA template the contrast null point occurs at different positions, at 60 and 75 Wt.% D_2O/H_2O , respectively (Figure 1). These results compare very well with the predicted values for scattering length density equivalents of Wt.% D_2O/H_2O for the silicalite structure in which a TPA molecule occupies each suitable crystal site. This confirms the role of the $R_g = 81 \text{ \AA}$ particles as crystal nuclei with the final zeolite crystalline density. There are still unexplained features, such as an aging effect prescribed by some patented preparations. On the basis of our results we believe that the chemistry behind aging before synthesis can be understood

4. Liquid Crystal Templates and MCM-41 Synthesis

In 1992 the Mobil Corporation extended the concept of template induced synthesis of zeolites by making silicate, aluminosilicate and other mesoporous structures using liquid crystals as templates. Use of liquid crystal templates opens up a realm of template action by surfactant mesophases to produce high surface area materials whose pore sizes are tens of Angstroms in diameter compared to the few Angstrom values of common zeolites. The techniques that we have developed above for small channel zeolites are appropriate for these new systems.

We have been investigating silica-only MCM-41 produced by the template action of the liquid crystalline hexagonal phase of cetyl trimethylammonium bromide (CTAB) in water[7]. A silica hexagonal framework is created after hydrothermal condensation of the silicate siloxyl groups. Calcining this mixture, leaves behind only this silica framework to give a hexagonal array of large diameter channels spaced at ca. 40 Å intervals.

The nature of these channels is more complex (Figure 2) than the initially assumed geometry of large diameter holes punched in a dense silica background. This has been defined using a variety of X-ray and neutron scattering experiments

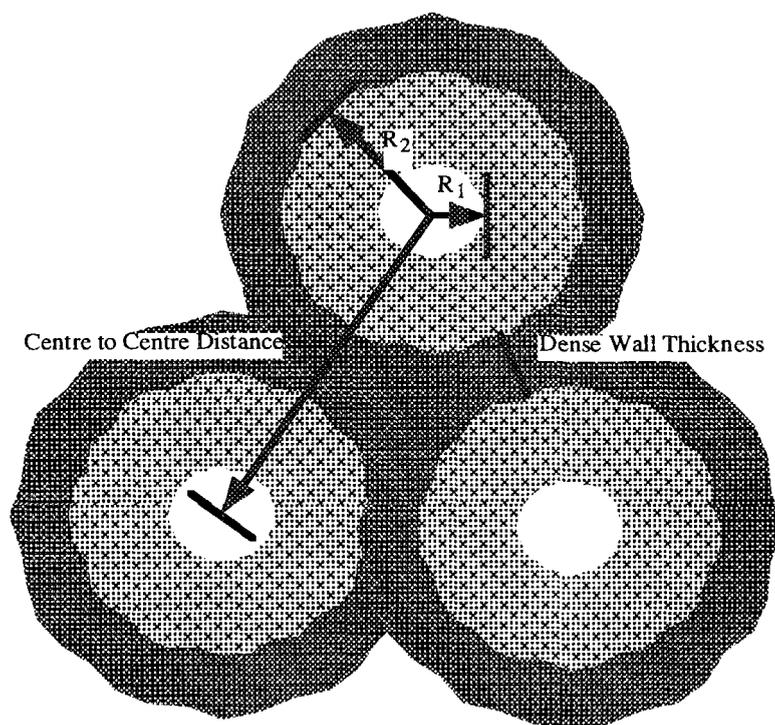


Figure 2 Model of the in plane structure of MCM-41 consistent with the form factor for synchrotron x-ray diffraction and the neutron small angle scattering contrast variation behaviour.

The synthesis gel of essentially three components - silica, water, and CTAB- has been optimised to give material with seven orders of the in plane diffraction seen in both synchrotron x-ray diffraction and neutron diffraction. A fitted form factor has allowed the silica density distribution in the calcined product to be defined. By using neutron small angle scattering at ISIS on LOQ with D₂O/H₂O mixtures for contrast variation, the model has been independently checked in both the template containing gel and the calcined product. Absorption of H₂ as a probe in the calcined material using both elastic and inelastic neutron scattering experiments has further supported the proposed structure.

These experiments produced a surprising result - the cylindrical void in the calcined material is much narrower than expected in projection- only about 7 Å in radius, not the 19 Å we expected. In addition the silica framework consists of two regions - a wall region as expected, and a spongy ring of silica of thickness about 12 Å surrounding the void. Both wall and ring are of surprisingly low density (ca. 1 Mg m⁻³) and are permeable to water and H₂ to more than 50% by volume.

The experiments on the synthesis "start" gel at room temperature show that the silica framework has already formed soon after mixing, and changes little on calcination. The pore is filled with CTAB, as is the 50% free volume in the spongy silica ring, but the walls contain little CTAB. This at least is not surprising and confirms that the mechanism of formation is indeed by silica decoration of the CTAB micelles in the liquid crystal.

With this new knowledge of the structure of the gel and calcined material it becomes possible to change the structure in desirable ways - larger empty pore regions for example- by variation of the composition of the initial synthesis gel.

6. Reflectometry and Templating at Surfaces

Templating at surfaces has been much discussed, indeed at least one model for the origin of life involves interactions at organic-silicate interfaces! We have just recently observed[8] the growth of very thin, highly oriented silicate films with mesoporous structure on the scale of 40Å produced by template induced growth at the air-water interface of concentrated surfactant solutions. X-ray reflectivity measurements show that the mechanism of this growth for our

preparation involves two stages. Neutron reflectivity, where the level of deuteration in the subphase and in the surfactant has been systematically changed provides a detailed picture of the structures at various stages of the synthesis. The formation of an organised surfactant layer at the interface in the first ten hours and the subsequent rapid growth of a structure which shows strong diffraction associated with the mesoporous repeat distance. The structure appears to grow when the interfacial layer is complete with a thickness of about 30 Å.

The experiments used a solution of cetyl trimethylammonium bromide (CTAB) dissolved in a minimal amount of methanol. This solution was stirred into approximately 20 times its volume of pure distilled water acidified with hydrochloric acid. Into this solution was added approximately 0.4g of tetraethoxysilane (TEOS) and the mixture stirred at room temperature for 15 minutes before being placed on the reflectometer. The solution was observed at room temperature in a clean flat dish containing approximately 30 millilitres of solution showing a positive meniscus. The sample environment was kept at constant humidity (saturation vapour pressure of water at the measuring temperature) by a continuous stream of humidified nitrogen. The reflectometer was programmed to take repeated scans over the Q range at approximately one hour intervals for two days.

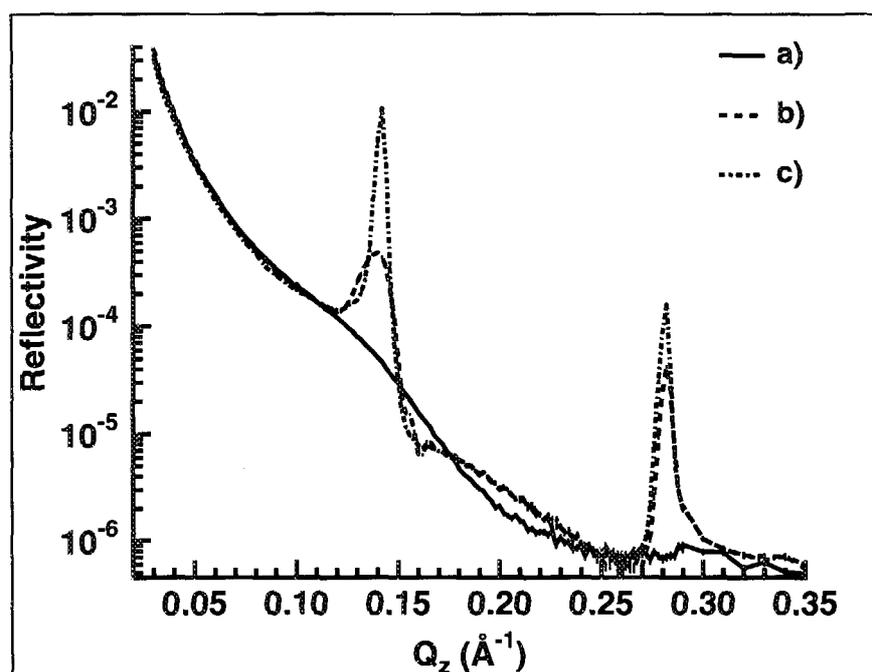


Figure 3. X-ray reflectivity from the air - water interface during the induction period showing the development of the reflectivity profile over time into diffraction peaks. a) 530

minutes, b) 608 minutes, and c) 687 minutes. (The neutron reflectivity changes in the same general way but the intensities are controlled by the level of deuteration in the components and hence give otherwise inaccessible structural information)

Figure 3 illustrates the very marked changes occurring in the reflectivity profiles as the reaction proceeds. In the earliest stages the reflectivity falls as approximately Q_z^4 and has superimposed Kiessig fringes which initially have a period $\Delta Q \sim 0.2 \text{ \AA}^{-1}$ (not shown in Figure 1) and which develop with time to $\Delta Q \sim 0.14 \text{ \AA}^{-1}$ (Figure 1a). This is immediately interpretable in qualitative terms as arising from a surface layer with an initial thickness ca 31 \AA which then increases to 45 \AA with time. After about 10 hours of "induction time", pronounced bumps appear at $Q_z = 0.142 \text{ \AA}^{-1}$ and 0.284 \AA^{-1} . These continue to grow, becoming sharper and more pronounced, as the reaction proceeds. By comparison with the induction period, growth of the "crystalline" diffraction peaks is fast. These peaks index on a repeat distance, a , of 44 \AA . The intensity of the first strong diffraction peak from the crystalline film has reached saturation within three hours of its appearance. Because of the humidity control, evaporation from the film over the time of the experiment was minimised.

This experiment mimics some of the processes used by nature to grow biological minerals such as silica and calcium carbonate. The genetic material is translated into proteins which either themselves act as templates or produce by enzymic action the substances which direct bio mineralisation. The multilayer structures produced in our results are accompanied in many cases by micron scale organisation reported by us previously [9] and which closely resemble biological forms described in reference [1].

7. Conclusions

The contrast variation possible with neutron scattering, the wide range of scattering vectors available with cold neutrons and the eventual availability of other contrast modes using polarisation analysis both for elastic scattering and inelastic scattering all suggest the continuing power of neutron methods into the twenty first century.

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