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Diffraction Studies of Alkyl- ammonium Vermiculites

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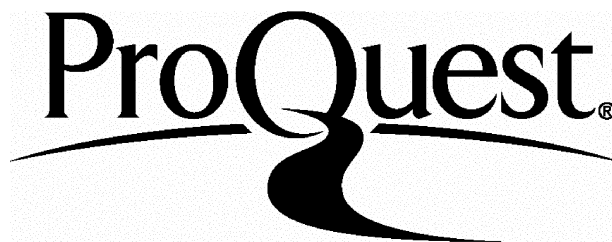
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Abstract

The aim of the research was to measure the structure developed at the interface between an aqueous liquid and a charged surface (the electrical double layer, EDL). Despite its importance in e.g. colloids, it had not previously been measured due to the lack of a suitable system. Macroscopically swollen vermiculite containing propyl-ammonium counterions was identified as a suitable system for such a measurement.

Vermiculite swelling behaviour was investigated as a function of salt concentration (c) and temperature, using neutron and X-ray diffraction. Small angle neutron scattering showed that the swollen vermiculite gels behave as typical colloids, exhibiting a layer spacing proportional to $c^{-1/2}$. Furthermore, it was discovered that the gels could be prepared with a layer spacing of $\sim 40\text{\AA}$, sufficiently small to allow measurement of the EDL structure by diffraction.

The EDL structure in the vermiculite gels was measured using time-of-flight neutron diffraction. Gels were prepared with several isotopic compositions and aligned with the scattering vector perpendicular to the clay layers. Difference analysis allowed location of both water molecules and counterions along the clay c^* axis. This was a novel treatment, allowing a principally liquid structure to be described by a single particle distribution function. It was found that two distinct layers of water molecules are associated with each of the clay surfaces and that the counterion density is greatest midway between the clay layers, in contrast to predictions based on the primitive model.

The same difference method was used to determine the interlayer structure in hydrated, unswollen crystals of butyl- and methyl-ammonium vermiculite, in order to clarify why swelling occurs only in propyl- and butyl-ammonium vermiculite. Butyl-ammonium ions are found to stand perpendicular to the clay surface while methyl-ammonium ions lie parallel. It is proposed that the larger counterions force the clay layers apart, weakening the clay-counterion Coulombic interactions.

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Standard Symbols and Abbreviations

b	Mean scattering length
b_{coh}	Coherent scattering length
b_{inc}	Incoherent scattering length
c^*	Axis perpendicular to the plane of the clay layers in a clay mineral ($\equiv z$ axis)
c_{ext}	The salt concentration in a solution in contact with a vermiculite gel
c_{int}	The salt concentration inside a vermiculite gel
c_{tr}	The excess (trapped) salt concentration in a clay crystal
c_{α}	Atomic fraction of species α
$C(Q)$	Self (single atom) scattering
CEC	Cation exchange capacity
d	The clay layer spacing in a clay mineral ($\text{\AA}$)
$D(Q)$	Distinct (interference) scattering
DCS	Differential cross section
DDCS	Double differential cross section
DLVO	DLVO theory of colloid stability proposed by Derjaguin, Landau, Verwey and Overbeek
E	Energy of a scattered quantum
E_0	Energy of incoming quantum
EDL	Electrical Double Layer
$F(Q, \omega)$	The total structure factor
$F(Q)$	The static total structure factor ($\equiv F(Q, 0)$)
$g(r)$	Radial distribution function

h	Planck's constant
$I(Q)$	Coherent scattering (Bragg intensity)
n_c	Number of carbon atoms in an alkyl group
Q	Scattering (or momentum transfer) vector magnitude
$S(Q)$	Crystallographic structure factor
T_c	The vermiculite gel to crystal phase transition temperature
ToF	Time-of-flight
z	Position on an axis perpendicular to a surface ($\equiv c^*$ axis)
θ	Scattering angle for a quantum scattered through an angle of 2θ
λ	Wavelength
$\rho(z)$	The total neutron scattering density as a function of position on the clay c^* axis
σ_{total}	Total scattering cross section
ω	Angular frequency
Ω	Solid angle into which scattering takes place

INTRODUCTION

1.1 Solid-Aqueous Solution Interfaces

Because of the ubiquity of water, its interaction with other species (hydration) is of great importance. In particular, the interface between a charged surface and an aqueous solution is central to a great number of systems and processes, including colloids (Hunter 1993), electrode reactions (Rose and Benjamin 1993), the behaviour of clay minerals (Brindley and Brown 1980) and the folding of proteins (Brett and Brett 1990). In fact, 'so many phenomena (are) dictated by hydration forces...that we might easily be persuaded that nothing else has any importance whatever' (Ninham 1985).

Unfortunately hydration has presented difficulties in experimental determination: Newton wrote of action-at-a-distance (i.e. hydration forces) 'that the concept represented so great an absurdity that any man who had in philosophical matters any competence whatever could hardly fall into it' (Ninham 1985). More recently there has been a tendency to use 'water structure...as a *deus ex machina*' to explain unexpected results, possibly as a result of its 'inaccessibility to direct experimental determination' (Israelachvili and Wennerström 1996).

Because of these difficulties, current understanding of the charged surface-aqueous liquid interface is largely based on theoretical treatments which simplify the problem by ignoring the water structure, treating it instead as a dielectric continuum (the primitive model). The first treatment was that of Helmholtz, in which the surface charge is balanced by a rigidly bound layer of counterions (Helmholtz 1879). This model gave

rise to the term Electrical Double Layer (EDL) to describe such an interface. Early this century the Gouy Chapman model introduced the concept of a diffuse distribution of ions away from the surface (Gouy 1910, Chapman 1913), and later these models were combined by Stern (Stern 1924; figure 1.1).

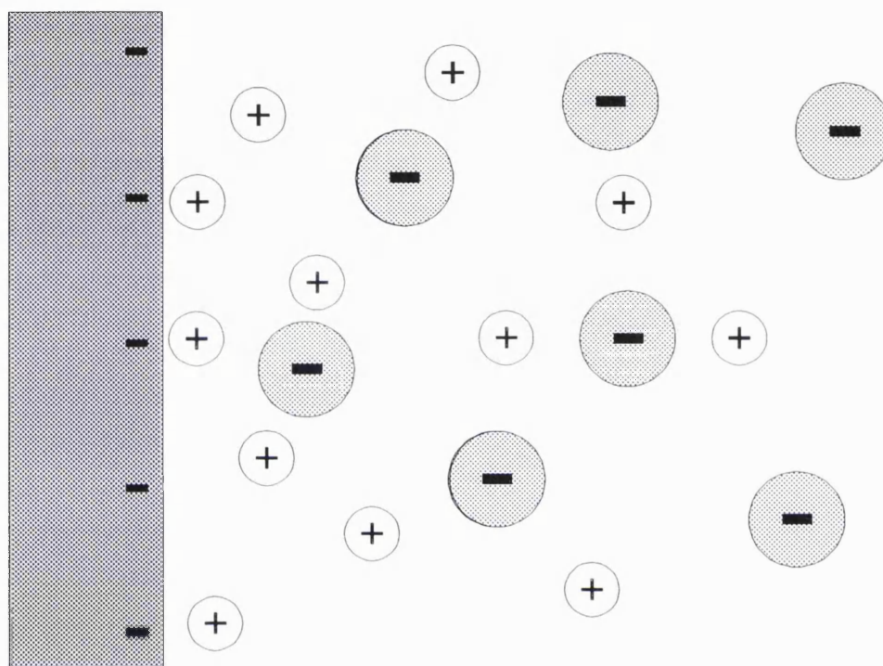


Figure 1.1. The Stern model, in which the surface charge is partially balanced by a layer of adsorbed counterions (the Stern layer). Beyond the Stern Layer the ion density normal to the surface is given by a Gouy-Chapman diffuse distribution, there being an excess of counterions and a deficit of coions near the surface. The model is primitive (solvent structure is ignored).

Current treatments of the EDL are still generally based on the primitive model, for example the DLVO (Derjaguin and Landau 1941, Verwey and Overbeek 1948) and Sogami (Sogami and Ise 1984) theories which predict the forces between colloidal particles dispersed in an electrolyte. While they have proved accurate at large interparticle separations there is evidence from clay swelling (Viani et al 1983), surface force measurements (Israelachvili and Wennerström 1996) and simulations (Marcelja

1997) that below $\sim 40\text{\AA}$ there is an additional repulsive force not predicted by these theories. In order to understand the limitations of the primitive model we need information on the structure developed in liquids at interfaces.

Evidence that the water structure near an interface is significantly different to bulk water structure has been provided experimentally, for example by thermodynamic methods and spectroscopy (Parsons 1990), and by computer simulations based on models which include the molecular nature of water (Spohr 1997 for example).

Despite the importance of the EDL structure however there has not previously been a direct measurement. This has principally been due to the problem of identifying a suitable sample. For a diffraction experiment the interfacial region has to give sufficient scattered intensity, the technique being inherently limited by intensity. In many samples the interface makes up a small fraction of the system (e.g. the interface between the bulk phases of an electrode and an electrolyte) or is irregular and poorly orientated (e.g. in many colloidal systems).

1.2 Thesis Content

The central result presented in this thesis is the first direct measurement of the electrical double layer structure in a colloidal system, made using neutron diffraction. The samples which were identified as suitable for this were vermiculite clay minerals, which consist of stacks of negatively charged aluminosilicate clay sheets with charge balancing counterions and water molecules located between the layers (figure 1.2).

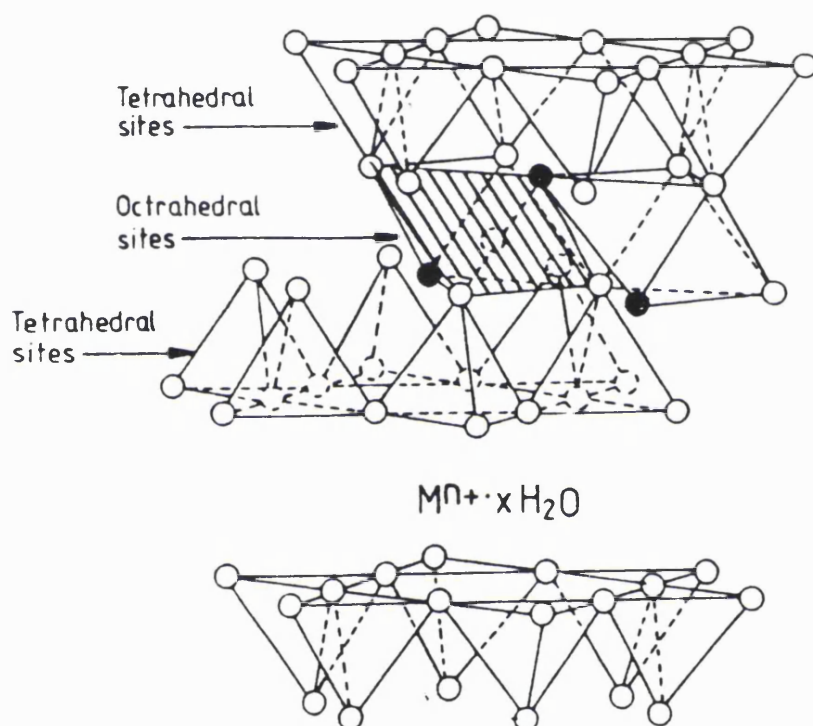


Figure 1.2. Diagram of a typical clay mineral, showing the layer structure and the location of counterions and water molecules between the clay layers.

Vermiculites have a regular separation between the clay layers, the clay layer spacing (d). Under certain circumstances they can absorb large quantities of water, expanding to form a gel with a clay layer spacing of 40-600Å (Garrett and Walker

1962). These macroscopically swollen vermiculites have many advantages for studying the structure of liquids at charged surfaces:

- The internal surface area is very large (typically $\sim 1000\text{m}^2\text{g}^{-1}$ in the samples studied), so a substantial fraction of the system consists of clay-liquid interfaces.
- The crystals are macroscopic ($\text{mm}^3\text{-cm}^3$) and the clay-liquid interfaces are highly orientated, the mosaic spread being typically 5° (Crawford et al 1991). It is therefore possible to align the sample with respect to a beam of radiation and a detector to measure the scattering density as a function of the perpendicular distance from the clay surface, simplifying analysis of the structure from three dimensions to only one dimension. In this orientation information on the structure parallel to the clay surface is lost, but the electrical double layer structure is expected to be manifested principally perpendicular to the surface (along the electric field gradient resulting from the surface charge).
- It was discovered that when the counterion is n-propyl-ammonium the vermiculite gels could be prepared with a regular clay layer spacing of $\sim 40\text{\AA}$. This is sufficiently small to conveniently measure by diffraction, but also sufficiently large to allow an electrical double layer structure to develop (Israelachvili and Pashley 1983, Rose and Benjamin 1991, Toney et al 1995 for example).

The double layer structure in these samples was investigated using time-of-flight (ToF) neutron diffraction, this method having two important advantages. Firstly, it is

possible to use hydrogen / deuterium substitution to label both water molecules and propyl-ammonium ions. The large difference in the neutron scattering lengths of the hydrogen and deuterium nuclei then allows the position of both water molecules and counterions to be identified. Secondly, by using ToF, data can be collected simultaneously over a very wide range of scattering vector magnitudes. This makes it possible to obtain very high real space resolution, down to 0.1Å in these experiments.

1.3 Thesis Layout

The thesis is laid out as follows. Chapters 2-4 contain background material: chapter 2 on aqueous solutions and the electrical double layer; chapter 3 on clay minerals; chapter 4 on neutron diffraction. Chapters 5-7 contain experimental details and results as follows: chapter 5, investigation of the interlayer structure in swelling and non-swelling alkyl-ammonium vermiculites, carried out with the aim of clarifying the mechanism of macroscopic swelling; chapter 6, experiments to characterise propyl-ammonium vermiculite; chapter 7, measurement of the electrical double layer structure in propyl-ammonium vermiculite. Note that, because the methods described in chapters 5 and 7 are similar, chapter 7 omits many experimental details, the reader being referred in the text to the necessary sections of chapter 5. The results are discussed in chapter 8 and chapter 9 contains the conclusion.

Chapter 2

The Structure of Aqueous Ionic Solutions and The Electrical Double Layer

2.1 Contents

This chapter describes the current view of water and its interaction with various species. This is followed by a summary of the various methods which have been applied to the problem of an aqueous solution interacting with a charged surface. The chapter is divided into five sections, covering i) the properties of the water molecule and bulk water, ii) the interaction of water with solute species (hydration), iii) theoretical models of the electrical double layer, iv) computer simulations of liquids at interfaces, v) experimental measurements on liquids at interfaces.

2.2 Water

2.2.1 The Water Molecule and Liquid Water

Aqueous systems exhibit distinctive features due to the unique properties of the water molecule. The model predicted by electron pair repulsion is that two bonding and two non-bonding electron pairs are arranged tetrahedrally around the oxygen atom. Because of the resulting high dipole moment (1.854D in the gas phase, Lide 1995) water molecules exhibit strongly preferred orientations in any polar or charged environment. Particularly favourable interactions can occur between a hydrogen atom and a non-bonded electron pair belonging to separate molecules, this interaction being called a

hydrogen bond. There is however no universal agreement on whether a hydrogen bond is fundamentally different to a strong dipole-dipole interaction. A working definition is generally adopted, for example 'A hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms' (Huheey 1983).

Because each water molecule contains two hydrogen atoms and two lone pairs of electrons on the oxygen atom, water molecules can form three dimensional structures based on an open tetrahedral network of hydrogen bonds. It is this network which gives water many of its characteristic macroscopic properties, for example high surface tension, maximum density at 4°C and decreased viscosity at high pressures (Ohmine and Tanaka, 1993).

Neutron diffraction experiments (Soper and Phillips 1986) indicate that the O-H bond length in liquid water is 0.98Å and that the intramolecular hydrogen-hydrogen distance is 1.56Å. The oxygen-oxygen pair distribution function has a very strong first maximum at 2.9Å and a weaker one at 4.5Å, the former giving a measure of the 'radius' of the water molecule. The oxygen-hydrogen distribution has strong peaks at 2.4Å and 3.9Å, showing orientational ordering of the molecules for hydrogen bonding.

The coordination number of water molecules has however been found in simulation studies to be between four and five (Corongiu and Clementi 1992, Ruocco et al 1993) showing that the ordering cannot be entirely tetrahedral. The coordination number in these simulations is also found to vary with temperature (Corongiu and Clementi 1992).

Radial distribution functions measured by diffraction are orientationally averaged. Computer simulations on the other hand have confirmed that individual molecules are tetrahedrally coordinated. Taking a single water molecule as the reference, four maxima are seen in the distribution of oxygen atoms around the reference molecule,

in positions corresponding to hydrogen bonding locations (Svishchev and Kusalik 1993, Kusalik and Svishchev 1994). The two maxima associated with the hydrogen atoms of the reference molecule are observed as separate entities, while those associated with the lone pairs of the reference molecule merge into each other. This indicates a rocking motion (libration) of the water molecules. These simulations have also identified the 'extra' coordination water as being non-tetrahedrally coordinated at a distance of 3.5Å.

This strong orientational ordering also has implications for the dynamics of liquid water, and evidence for collective rearrangements of ~20 water molecules on a timescale of $<10^{-12}$ s have been observed in both computer simulations and inelastic neutron scattering experiments (Ohmine and Tanaka 1993).

2.2.2 Ice

In the solid phase water can adopt a variety of structures (Franks 1986). At atmospheric pressure ice Ih is formed, in which water molecules are tetrahedrally coordinated to four nearest neighbours, the oxygen-oxygen distance being 2.76Å. This leads to an open structure, which is exceptional in being less dense than liquid water. The water molecules are arranged in hexagonal rings, with a chair conformation in one plane and a boat conformation in the perpendicular plane. This leads to columns of hexagonal rings. Although the molecules are all orientated for hydrogen bonding the protons on individual molecules are not consistently orientated in the same direction. At higher pressures and lower temperatures ice has a variety of distorted tetrahedral structures, all of which are denser than the liquid.

2.3 Hydration

2.3.1 Hydration of Charged and Polar Species

The interaction of water molecules with charged or polar species (hydrophilic hydration) is dominated by Coulombic interactions. Metal ions in solution form complexes with the generic formula $M(H_2O)_n^{z+}$, in which the ion is surrounded by a coordination shell of orientated water molecules. The existence of these complexes has been demonstrated both by diffraction and by computer simulations in a wide variety of systems (Marcus 1988).

The coordination number is typically six (octahedrally coordinated), but four has been reported for smaller monovalent ions such as Li^+ and Na^+ and up to ten for larger di- and trivalent ions (Marcus 1988). The average lifetime of a water molecule in these complexes also increases with the charge density of the ion and ranges from $>10^6$ s in $Cr(H_2O)_6^{3+}$ to $<10^{-10}$ s in $Cu(H_2O)_6^{2+}$. Hydration complexes can also form around anions but tend to be relatively unstable, with an average lifetime $<10^{-10}$ s (Friedman 1985).

Formation of these complexes is favoured by the Coulombic interactions between the cations and the oxygen atoms of the water molecules. Complex formation is however entropically unfavourable because of the increased ordering imposed on the water molecules. Both these effects increase with increasing charge density of the cation, the overall free energy of formation becoming more favourable (Lynden-Bell and Rasaiah 1997). Cations with a high charge density (eg Li^+) therefore tend to retain their first hydration shell and are termed structure making, while cations of low charge density (eg K^+) are more readily dehydrated and are termed structure breaking.

A general model for the longer range effect of the ion on water structure was proposed by Frank and Wen (1957), identifying three regions around an ion (figure 2.1). The first region (A) consists of water molecules whose arrangement is determined principally by the influence of the ion. This is not necessarily limited to the primary hydration shell described by a coordination complex. There is then a disordered region (B) between the region of water ordering around the ion and the region of bulk ordering (C). The extent of each of these regions will depend on the size and charge of the ion.

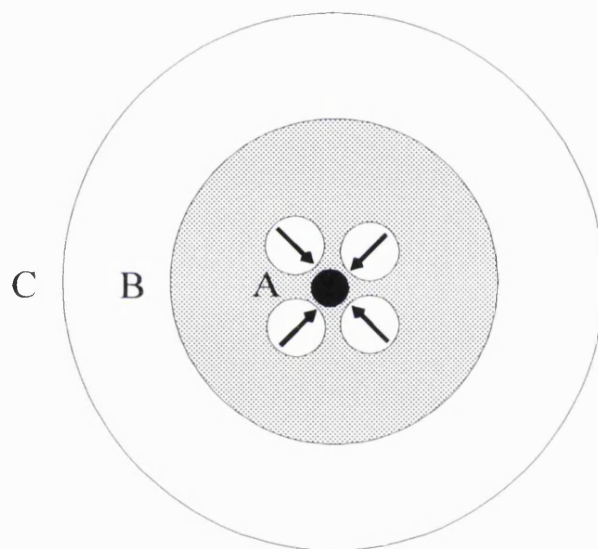


Figure 2.1. The Frank-Wen model for describing water around a hydrated ion.

2.3.2 Hydration of Non-Polar Species

Non-polar species cannot form hydrogen bonds. When such species are hydrated reorientation of the water molecules occurs to minimise disruption of the hydrogen bond network. This is termed hydrophobic hydration and leads to the formation of clathrate or cage-like arrangements of hydrogen bonded water molecules around the hydrated species. While hydrophobic hydration can be enthalpically favoured it is generally entropically unfavourable due to the ordering imposed on the water molecules. This is reflected for example in the free energies of transfer to water for hydrocarbons. These are found to be proportional to the surface area of the molecule, which in turn is proportional to the number of water molecules that must reorientate during hydration (Israelachvili 1990).

Computer simulations which vary the charge of a single hydrated ion while keeping its size constant have illustrated the relationship between charge and entropy of hydration (Lynden-Bell and Rasaiah 1997). At charges of $\sim +0.3e$ there is found to be a minimum in the entropy of hydration, corresponding to hydrophobic hydration. As the charge on the ion is made either more positive or more negative the entropy change passes through a maximum before decreasing again, the decrease being due to the formation of a strongly ordered hydration shell around the highly charged ion. It should therefore be noted that, although they involve very different mechanisms, both hydrophobic and hydrophilic hydration tend to be entropically unfavourable and enthalpically favourable.

Clathrate cages occur as both short-lived arrangements in the liquid phase and as crystalline solids. The latter have a variety of ice-like structures which are determined by the size of the hydrated species (Englezos 1993). The basic structural unit in crystalline

clathrates is a pentagonal dodecahedron formed by twenty water molecules, which is large enough to accommodate a methane molecule. Larger cavities are created as a result of the packing of this structural unit, and clathrates cages can contain larger hydrocarbons and noble gases.

Because of the entropic cost of hydrophobic hydration, many non-polar molecules are immiscible with water. This effect is responsible for the rich variety of behaviour observed in certain molecules containing both polar and non-polar groups. These molecules, called surfactants, are soluble in water at low concentrations ($\sim 10^{-4}\text{M}$), but above a certain concentration they assemble into structures which leave only the polar groups in contact with the water molecules. This occurs above a specific concentration (the critical micelle concentration, or CMC), this concentration depending on the surfactant species. Common examples of surfactants include $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ and $\text{C}_{17}\text{H}_{35}\text{CO}_2^-$. The assembled structures include micelles (spherical or tube like assemblies in which the polar groups sit on the surface) and bilayers (sheets in which the polar groups sit on both surfaces). Non polar molecules such as alkanes can also be incorporated into these structures (Hunter 1993).

Hydrophobic hydration can be strongly temperature dependent, as at higher temperatures the entropic cost to the free energy of hydration can outweigh the enthalpic gain. This is manifested in a transition temperature above which a particular species is immiscible with water: the denaturing of proteins at high temperatures is one example of the complicated structural changes this can cause.

2.4 Theoretical Models of The Electrical Double layer

The structure of the electrical double layer in an aqueous system is determined by hydration of both the surface and of the species in solution. Because of its complexity and the difficulties of direct measurement the problem was initially treated theoretically, using primitive models which ignore the water structure. The development of these models is outlined in this section. For more information on these models refer to *Electrochemistry: Principles, Methods and Applications* (Brett and Brett 1993).

2.4.1 The Compact Double Layer

The first and simplest model of the interfacial region between a charged solid surface and an electrolyte was developed by von Helmholtz in the late 19th century. In the Helmholtz model the excess counterions in the solution which balance the surface charge are all located in a rigid layer at the interface (figure 2.2) with the double layer interactions extending no further than this. This is the origin of the expression ‘electrical double layer’. The counterions are considered to be located at a distance from the surface equal to their actual ionic radius, but are treated as point charges. The situation is in fact analogous to a parallel plate capacitor, one plate being located at the surface and the other at the plane of counterions, and gives a linear decay of electrostatic potential away from the surface. The model is very simple in neglecting any interactions occurring further into solution than the counterion layer. It also neglects any dependence on the electrolyte concentration.

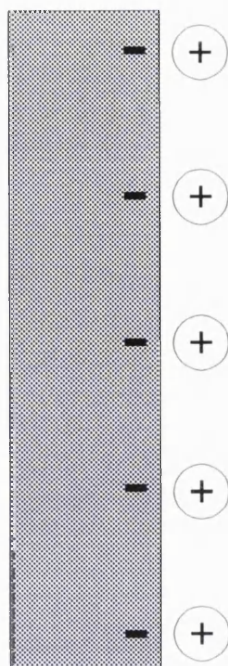


Figure 2.2. The Helmholtz model of the electrical double layer, in which the surface charge is balanced by a layer of rigidly bound counterions.

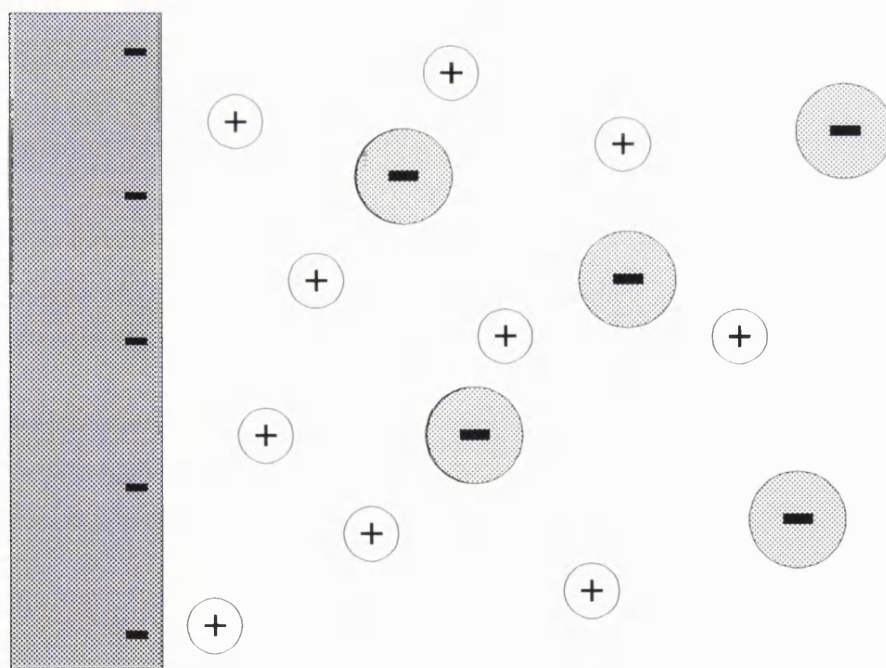


Figure 2.3. The Gouy-Chapman model for a negatively charged surface, in which the ion density normal to the surface is given by the Poisson-Boltzmann distribution (equation 2.1). The solvent structure is ignored.

2.4.2 The Diffuse Double Layer

A more sophisticated model was developed independently by Gouy in 1910 and Chapman in 1913. This model was based on thermodynamic interpretation of surface tension (electrocapillary) measurements (Crow 1994) of mercury electrodes in contact with an electrolyte. The Gouy Chapman model introduced the concept of a ‘diffuse’ double layer in which the ions in solution have a probability distribution arising from their thermal motion and the electric field gradient due to the surface (figure 2.3).

The ion distribution is given by the Poisson-Boltzmann distribution

$$n_i = n_i^0 \exp\left\{\frac{-z_i e \phi_x}{kT}\right\} \quad (2.1)$$

where n_i^0 is the cation or anion density (assuming the electrolyte is symmetrical) in the bulk solution, n_i the density at a position where the potential is ϕ_x , e is the charge of the electron and z_i the integral number of charges on each ion. The total charge density at a distance x from the surface is given by

$$\rho(x) = \sum_i n_i^0 z_i e \exp\left\{\frac{-z_i e \phi_x}{k_B T}\right\} \quad (2.2)$$

The charge distribution and potential are then related by the Poisson Equation:

$$\frac{d^2 \phi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon_0 \epsilon_r} \quad (2.3)$$

Integrating equation 2.3 in the limits $0 < x < \infty$, representing the region from the surface to the bulk solution, gives (Brett and Brett 1993)

$$\frac{\tanh(ze\phi_x/4k_B T)}{\tanh(ze\phi_0/4k_B T)} = \exp\left(\frac{x}{\kappa}\right) \quad (2.4)$$

where ϕ_0 is the surface potential and κ is the Debye length, given by

$$\kappa = \left(\frac{\varepsilon_0 \varepsilon_r k_B T}{2 n_i^0 z^2 e^2} \right)^{\frac{1}{2}} \quad (2.5)$$

where ε_0 is the permittivity of vacuum and ε_r is the relative permittivity of the solvent.

The Debye length therefore gives the distance at which the surface potential has dropped by a factor of $1/2.718$, and can be used as a measure of the ‘thickness’ of the electrical double layer (Everett 1988). The Debye length is concentration dependent, the extent of the diffuse double layer increasing with decreasing concentration in the electrolyte. For water at 298K, $\kappa = 3.04 \times 10^{-8} z^{-1} c^{-\frac{1}{2}}$ cm, so with a monovalent electrolyte the Debye length is $3.0\text{\AA}$ for 1M, $9.6\text{\AA}$ for 0.1M and $30\text{\AA}$ for a 0.01M electrolyte.

This model takes into account the effect of electrolyte concentration and surface charge, although the ions are treated as independent point charges (the mean field model). Structural effects of the solvent are also still ignored.

2.4.3 Further Models of The Diffuse Double Layer

A model which combined the concepts of the Helmholtz and Gouy Chapman models was developed by Stern in 1924. In the Stern model the electrical double layer is divided into two regions. The region close to the surface, where the potential is highest and the approximations of the Gouy Chapman model are least applicable, is considered to consist of a layer of adsorbed counterions (the Stern layer), while the remainder are distributed in a Gouy Chapman type diffuse layer. The plane dividing these two regions is referred to as the Outer Helmholtz Plane (OHP).

The Stern model was expanded by Grahame in 1947 to distinguish between contact adsorbed ions and ions which retain their hydration shell. The dipolar nature of

the solvent is also included in the Bockris Devanathan Muller model (Brett and Brett 1993). The double layer in this model consists of three components (figure 2.4).

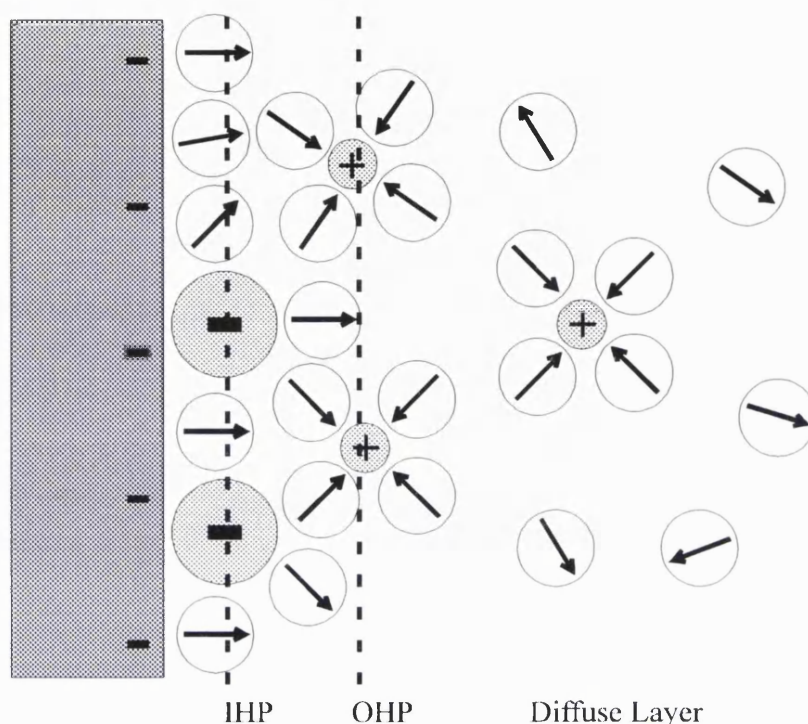


Figure 2.4. The Bockris Devanathan Müller model of the EDL showing i) the orientation of solvent dipoles, and ii) the presence of solvated and unsolvated ions at the surface.

In contact with the surface is a layer consisting of dipole orientated solvent molecules and specifically adsorbed ions which have lost their first solvation shell, the extent of this layer being defined by the Inner Helmholtz Plane (IHP). Beyond the IHP are located ions which retain their solvation shells, this layer being defined by the OHP. Finally there is a Gouy Chapman type diffuse double layer.

More recent models based on the diffuse distribution include the Modified Gouy-Chapman (MGC) model which incorporates a plane of closest approach to the surface (Greathouse et al 1994) and the Restricted Primitive Model (RPM) in which the ions are treated as hard spheres (Patra and Ghosh 1994).

2.4.4 Limitations of the Primitive Model

Theories such as DLVO (Derjaguin and Landau 1941, Verwey and Overbeek 1948) make predictions of the interaction of surfaces based on primitive models of the intervening solution. These have however been proved to be unreliable for surface separations less than $\sim 40\text{\AA}$ (Israelachvili and Wennerstrom 1996).

To understand this limitation we need detailed structural information for the electrical double layer. Experimental studies as well as computer simulations based on molecular models have provided extensive evidence for solvent structuring at surfaces. These results are summarised in sections 2.5 and 2.6 below. Models have also been developed based on statistical mechanical treatments which include the molecular nature of the solvent. These models predict layering of solvent molecules at surfaces for a range of concentrations and surface charges (Tang et al 1992, Patra and Ghosh 1994).

2.5 Computer Simulations of Liquids at Surfaces

Computer simulations which model the molecular nature of the solvent have provided evidence of substantial restructuring of water near surfaces. Molecular dynamics simulations (Spohr 1997) show a degree of layering of water molecules even at uncharged, structureless surfaces. This effect becomes more pronounced at structured surfaces. Water at a platinum surface (Spohr 1989) has three oscillations of decreasing magnitude in the oxygen density profile perpendicular to the surface, the first occurring at $2.5\text{\AA}$ from the surface. Parallel to the surface the first water layer forms a regular array. The water molecules sit with their dipole moment roughly parallel to the surface, indicating that maintaining hydrogen bonds between water molecules is more important than optimising the water-platinum interactions. Similar layering is seen in simulations of solutions of LiF (aq) at a mercury surface (Eck and Spohr 1997). Two layers of water molecules are observed in Monte Carlo simulations of water confined between uncharged clay surfaces (Bridgeman and Skipper 1997), although no restructuring of the water is seen beyond this.

Simulations of water confined between platinum surfaces with a separation of $40\text{\AA}$ show one strongly ordered layer and two weaker layers of water molecules associated with each surface. Beyond this the water structure is unperturbed (Xia et al 1995). In this study an applied field of $1\text{V}\text{\AA}^{-1}$ (corresponding to a surface charge density of $8.85 \times 10^{-2}\text{Cm}^{-2}$) created little difference in the water structure, but a field of $2\text{V}\text{\AA}^{-1}$ caused almost total layering of the water molecules. This structure is however hypothetical as in reality dissociation of the water molecules into ions would occur. Simulations of NaCl solutions between Pt surfaces with a separation of $25\text{\AA}$ also show three layers of water molecules, the structure of the central $10\text{\AA}$ region being

unperturbed (Rose and Benjamin 1991). Application of a field of up to $1\text{V}\text{\AA}^{-1}$ resulted in partial layering across the whole of this region (Rose and Benjamin 1993). The structure of the hydration shells of the ions was not found to be significantly affected by the presence of the surface.

Simulations also show the importance of hydration effects in determining the ion distribution perpendicular to a surface. Simulations of 0.3M LiF (aq) and 0.3M LiI (aq) at an uncharged metal surface show that both lithium and fluoride ions are broadly distributed between $5\text{\AA}$ and $13\text{\AA}$ from the surface. Iodide ions, which have a lower charge density and so are less strongly hydrated, are contact absorbed at the surface (Philpott et al 1995). This contrasts with Monte Carlo simulations based on primitive models which give a monotonic decay of the ion distribution as a function of distance from the surface (Torrie and Valleau 1979).

2.6 Experimental Studies of Liquids at Surfaces

Traditional models such as those of Gouy Chapman and Grahame were based on experimental observations of macroscopic properties (eg capacitance), mainly for the Hg / electrolyte interface ('nearly everything one desires to know about the electrical double layer is ascertainable with mercury surfaces if it is ascertainable at all'; attributed to Grahame, Trasatti 1995).

There has not previously been a direct measurement by diffraction of an electrical double layer, although an attempt was made by Soper and Gromek (unpublished results) using a sodium montmorillonite clay. Due to the poor orientation of the sample and the limited momentum transfer range of the data they were unable to confidently assign a structure.

Since the early 1970's however, various techniques have been developed to obtain microscopic information on the electrical double layer structure. Examples of results obtained for both aqueous and non-aqueous solutions at a variety of surfaces are given in this section.

2.6.1 Spectroscopy

Because of its sensitivity to low concentrations of ions spectroscopy has been the main experimental method for *in situ* studies of the electrical double layer since around 1970 (Parsons 1990). While there are a wide variety of methods (Gutiérrez and Melendres 1990) they all depend on observing the changes in energy levels which are caused by the chemical environment, showing whether a particular species is absorbed on a surface and how it is orientated. It is also possible to investigate changes induced in the structure, for example by changing an applied potential or the electrolyte

concentration. Spectroscopic techniques have been most commonly used to study electrodes, often in contact with non-aqueous electrolytes, and have provided evidence for the preferential orientation of a wide variety of species at the electrode surface.

One method which has been extensively used (Tian et al 1995) is surface enhanced Raman spectroscopy (SERS). The Raman effect is the change in wavelength of radiation resulting from gain or loss of energy to the vibrational or rotational modes of a molecule. SERS relies on the discovery (Fleischmann et al 1973) that absorption of molecules at surface sites can cause enhancement of the Raman effect by a factor of up to 10^6 . This has allowed studies of interfaces which make up only a small part of a system. It has however been shown that the effect is associated with specific sites and so may not be reliable in giving the general properties of the surface (Furtak 1994).

Tian et al (1994) have studied solutions of NaClO_4 (aq) at a silver surface with an applied potential of -0.2 to -2.0V. The frequency of the peak due to O-H stretching was found to increase with the applied potential, indicating both that water molecules are present on the surface and also that their orientation is affected by the surface charge. Evidence of the interfacial water structure being potential dependent has also been seen with platinum surfaces (Probst and Thull 1995).

SERS has also shown that the choice of surface can affect the double layer structure. Tian et al (1995) compared a 3M KCl (aq) electrolyte on silver and gold surfaces with negative applied surface potentials. They found that, although in both cases the intensity of the metal-Cl and O-H vibrational peaks are potential dependent, the maximum intensities occur at different potentials in the two systems. The absorption of CN^- onto Pt(111) and Pt(110) surfaces is also found to be both surface and potential dependent (Friedrich et al 1995).

The effect of cation size has been investigated by SERS (Zou et al 1997),

comparing aqueous solutions containing Li^+ , Na^+ , K^+ and Cs^+ at surfaces with negative applied potentials. They proposed that Li^+ maintains a full first hydration shell but that as the size increases along this series the cations begin to dehydrate and come into direct contact with the electrode surface. This reflects the weaker hydration of the larger (structure breaking) ions.

Evidence of preferential orientation of solvent molecules and ions has also been seen in non-aqueous solutions. Acetonitrile molecules (CH_3CN) at a platinum surface are found to sit with the C-N bond perpendicular to the surface (bonding through the electron pair of the nitrogen) if a positive potential is applied to the surface, but parallel to the surface if a negative potential is applied (Marinkovic et al 1996).

Electron spectroscopy, which probes transitions between electronic states of individual atoms, has been used to compare the intensities of bands arising from each species at the liquid - vacuum interface. Studies of K^+ and Cs^+ octanoate and 8-iodo octanoate in formamide (CHONH_2) have shown (Bökman et al 1992) that the number of anions at the surface is greater than the number of cations. The number of ion pairs at the surface was also found to be greater than in the bulk solution.

2.6.2 Surface Force Measurements

Information on the structure perpendicular to the interface can be inferred from surface force measurements. In one of the original experiments the force between two mica surfaces immersed in a solution of KCl (aq) was measured as a function of the surface - surface separation (Israelachvili and Pashley 1983). At separations greater than $\sim 30\text{\AA}$ this was found to be in good agreement with theories based on primitive models of the diffuse double layer (Derjaguin and Landau 1941, Verwey and Overbeek 1948).

At smaller separations however a strong repulsion was observed which increased exponentially with decreasing separation. At separations less than $\sim 15\text{\AA}$ a series of oscillations was observed, the force alternating between attractive and strongly repulsive. Five distinct oscillations of increasing magnitude were observed as the separation was decreased. These had a periodicity of $2.5 \pm 0.3\text{\AA}$, interpreted as the radius of the water molecule. This suggests the presence of ordered layers of water between the surfaces. Similar effects have been observed with a variety of surfaces and confined species, including non-polar molecules such as alkanes (Israelachvili 1990). The origin of this ordering must therefore be partly steric in nature, rather than purely due to electrostatic interactions between the solvent and the surface. These results again illustrate the importance of solvent structure in determining interfacial structure.

2.6.3 Reflectivity

Reflectivity measurements can give information on the liquid structure perpendicular to a surface. Toney et al have used X-ray reflectivity to fit an oxygen density profile perpendicular to the interface for 0.1M NaF (aq) at an Ag(111) surface with applied potentials of -0.23V and +0.52V (Toney et al 1995). With the negative potential three maxima are seen with a periodicity of $2.6\text{\AA}$, the first occurring at $3.7\text{\AA}$ from the plane of the surface Ag nuclei. With the (larger) positive potential four oscillations are seen with a periodicity of $2.8\text{\AA}$. A shift towards the surface is also observed, the first peak occurring at $2.7\text{\AA}$. This indicates that i) water molecules were present in the form of layers, and that ii) the water molecules reorientate with an applied field, the hydrogen and oxygen atoms being adjacent to the surface with negative and positive applied fields respectively.

2.7 Summary

Experiments and computer simulations have both illustrated that the interaction of water molecules with each other and with other species can lead to significant restructuring of aqueous solutions at interfaces. Current treatments of the electrical double layer are unrealistic, in that they generally ignore the molecular properties of the water molecules. This is reflected in the failure of theories such as DLVO to predict the interactions between surfaces at separations less than 40Å. In order to understand these we need detailed structural information on the electrical double layer.

Chapter 3

Clay Minerals

3.1 Contents

This chapter gives an introduction to clay minerals, which were used to investigate the electrical double layer structure. More detailed information can be found in *X-Ray Diffraction and the Identification and Analysis of Clay Minerals* (Moore and Reynolds 1989), *Crystal Structure of Clay Minerals and their X-Ray Identification* (Brindley and Brown 1980) and *Chemistry of Clays and Clay Minerals* (Newman 1987).

3.2 Introduction to Clay Minerals

3.2.1 The Clay Layer

The defining feature of clay minerals (phyllosilicates) is that they consist of layers constructed from two structural units. The first unit is the MO_4 tetrahedron. These are corner-linked into an infinite two dimensional sheet (figure 3.1). The shared (basal) oxygen atoms lie in a single plane (the basal plane) and are arranged around hexagonal cavities in the sheet structure. The unshared (apical) oxygen atoms form another plane. The second unit is the MO_6 octahedron. These are edge-linked to form an infinite two dimensional sheet (figure 3.2). This sheet can also be visualised as two planes of close packed oxygen atoms, with cations sitting in the octahedral holes.

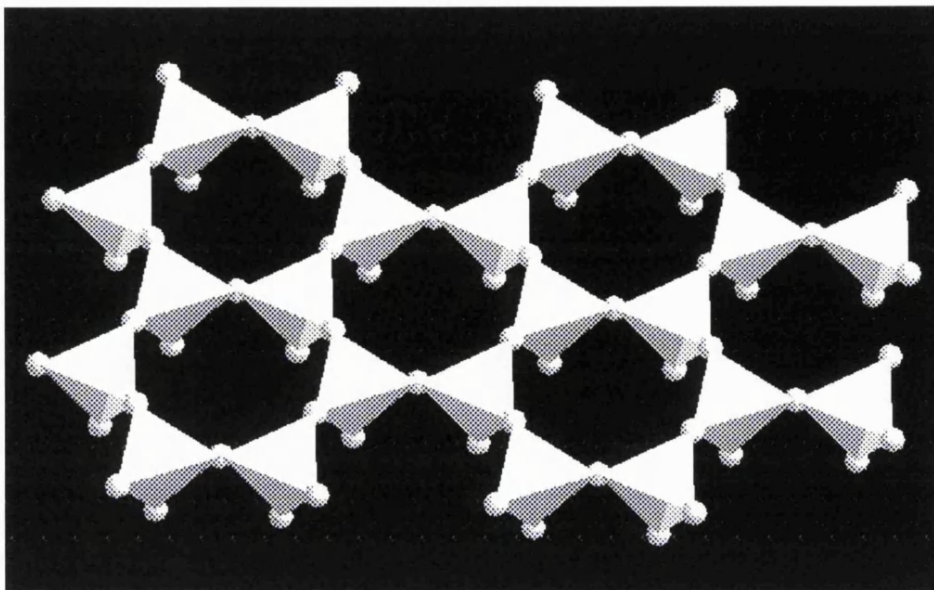


Figure 3.1. Part of a sheet constructed from corner sharing MO_4 tetrahedra. Oxygen atoms are shown as spheres, the cations being located at the centre of the tetrahedra. The sheet is viewed looking down onto the plane of basal oxygen atoms with the apical plane of unshared oxygen atoms below. The cations form a third parallel plane. Note that the arrangement of the basal oxygen atoms leads to hexagonal cavities on the surfaces of clay minerals.

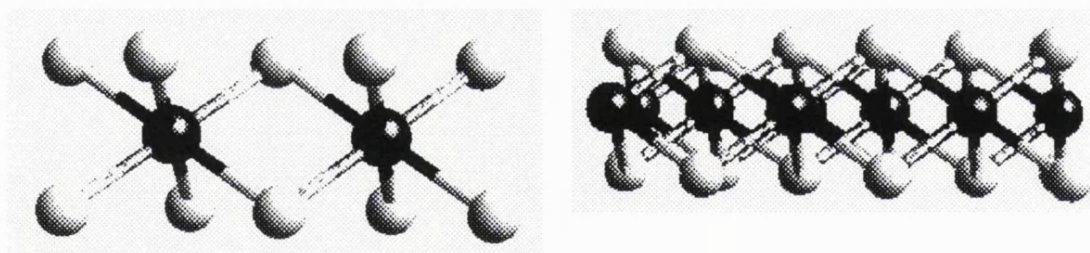


Fig 3.2. Two pictures illustrating the octahedral sheet structure. The left hand picture shows a pair of edge sharing MO_6 octahedra, with cations shown in black and oxygen in white. The picture on the right shows how these form a sheet with the atoms lying in three parallel planes.

Clay minerals consist of stacks of clay layers, the layers being constructed by joining several sheets. The oxygen-oxygen distance is similar in the tetrahedra and the octahedra, so it is possible to join a tetrahedral and an octahedral sheet by sharing two out of the three oxygen atoms forming one face of each octahedron with the apical oxygen atoms of the tetrahedra. The structure formed is called a tetrahedral-octahedral or 1:1 layer. A second tetrahedral sheet can be joined to the other face of the octahedral sheet to give a tetrahedral-octahedral-tetrahedral or 2:1 layer (figure 3.3). Both 1:1 and 2:1 structures can contain distortions caused by a mismatch in the dimensions of the tetrahedral and octahedral sheets. In all clay layers the unshared oxygen atoms of the octahedral sheet occur as hydroxyl groups, which sit below hexagonal cavities in the tetrahedral sheets. The orientation of the hydroxyl group can be either parallel or perpendicular to the plane of the clay sheet (Serratosa and Bradley 1958).

Electrical neutrality of the clay layer can be achieved in two ways. All of the tetrahedral sites are occupied by silicon and either i) all of the octahedral sites contain a divalent cation (trioctahedral clays), or ii) two thirds of the octahedral sites contain a trivalent cation, leaving one third vacant (dioctahedral clays). The most common cations found in clay minerals are Si in the tetrahedral sheet and Mg or Al in the octahedral sheet.

A negative charge on the sheet can occur if these cations are substituted by others with a lower valency, with overall electrical neutrality being maintained by charge balancing counterions located between the clay layers. In the tetrahedral sites Al^{3+} or Fe^{3+} can substitute for Si^{4+} , while a wide variety of ions have been observed in the octahedral sites including Li^+ and most of the transition elements (Newman 1987). Vacancies can also occur in the octahedral sites.

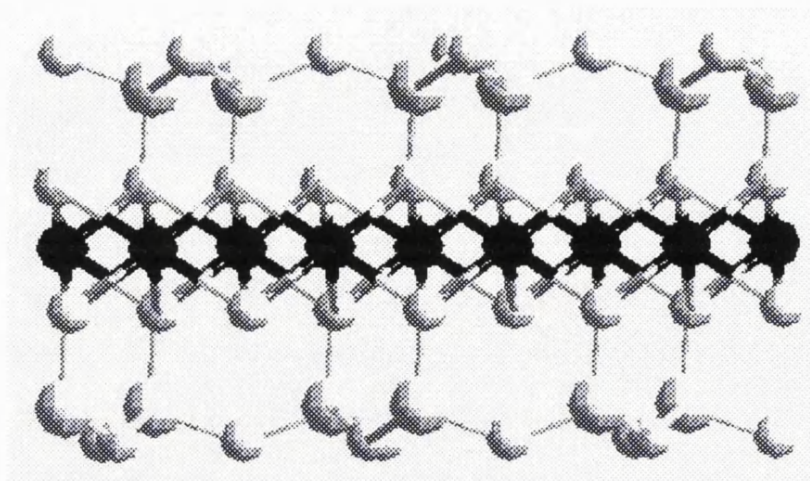


Figure 3.3a. Part of an assembled 2:1 clay layer, formed from an octahedral sheet and two tetrahedral sheets by sharing the apical oxygen atoms of the tetrahedra with two thirds of the octahedral oxygen atoms. Octahedral cations are shown in black, oxygen (small spheres) and tetrahedral cations (large spheres) in white. This figure shows how one third of the octahedral oxygen atoms are not shared with the tetrahedral layer. These exist as hydroxyl groups.

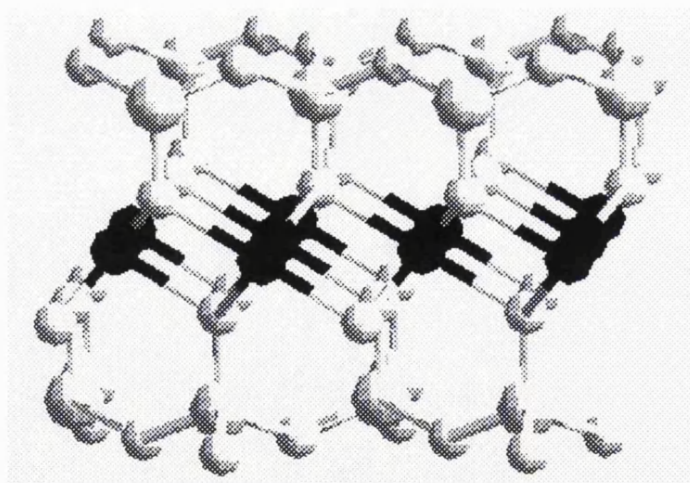


Figure 3.3b. Another view of part of a 2:1 clay sheet, rotated by 90° around an axis perpendicular to the layer and tilted forward to show the hexagonal arrangement of the surface oxygen atoms. The upper part of this figure shows how the hydroxyl groups are located below the hexagonal cavities in the clay surface.

The dimensions of the unit cell of a 2:1 layer are typically of the order of 4Å to 10Å along the a and b axes (in the plane of the clay layer) and $\sim 8\text{\AA}$ along the c axis, depending on the cations present in the layer. It should be noted that the c axis of the unit cell is not orthogonal to the plane of the clay layer, and a useful dimension for categorising clay minerals is the c^* axis, the projection of the c axis perpendicular to the clay layer.

We can define a fractional negative charge, x , as the charge per $\text{O}_{10}(\text{OH})_2$ unit of clay in a 2:1 mineral. 1:1 minerals usually have low or zero layer charge, while in 2:1 minerals the layer charge can be from $x = 0$ to $x \sim 1$, corresponding to a surface charge density of $0 \sim 0.3\text{Cm}^{-2}$. Clay minerals with a high layer charge (eg micas, vermiculites) tend to occur as macroscopic crystals of $\sim\text{cm}^3$, while crystals of low or zero charged clay minerals (eg talc) occur with μm dimensions. Strictly speaking the term clay refers to any geological material with a particle size of $<2\mu\text{m}$, clay minerals being the main component of clays. In this thesis however clays should be assumed to mean clay minerals.

Table 3.1 lists some of the important clay minerals divided into groups by layer type and charge (Newman 1987). Because of the continuous variation between clay minerals these groups are general categorisations rather than absolute divisions. The somewhat arbitrary division of smectites and vermiculites on the basis of layer charge is an example of this. The relatively weak interactions between the clay layers means that clay layers of different sorts can also be found stacked together. An example of this is smectite-illite interstratification, which occurs because buried smectites are transformed into illite by the replacement of Si^{4+} by Al^{3+} and K^+ in the clay layers (Newman 1987).

Group	Type	Unit Formula	Charge	Species
Kaolinite	1:1 di	$Y_4Z_4O_{10}(OH)_8$	0	Kaolinite, nacrite
Serpentine	1:1 tri	$Y_6Z_4O_{10}(OH)_8$	0	Chrysotile, antigorite
Pyrophyllite	2:1 di	$Y_2Z_4O_{10}(OH)_2$	0	Pyrophyllite
Talc	2:1 tri	$Y_3Z_4O_{10}(OH)_2$	0	Talc, willemite
Micas	2:1 di	$Y_2Z_4O_{10}(OH)_2$	1	Muscovite, paragonite
	2:1 tri	$Y_3Z_4O_{10}(OH)_2$	1	Phlogopite, biotite
Chlorites	2:1 di	$Y_2Z_4O_{10}(OH)_2$	Variable	Donbassite
	2:1 tri	$Y_3Z_4O_{10}(OH)_2$	Variable	Clinochlore, chamosite
Smectites	2:1 di	$Y_2Z_4O_{10}(OH)_2$	0.25-0.6	Saponite, hectorite, sauconite
	2:1 tri	$Y_3Z_4O_{10}(OH)_2$	0.25-0.6	Montmorillonite, bentonite
Vermiculites	2:1 di	$Y_2Z_4O_{10}(OH)_2$	0.6-0.95	Dioctahedral vermiculites
	2:1 tri	$Y_3Z_4O_{10}(OH)_2$	0.6-0.95	Trioctahedral vermiculites

Table 3.1 Classification of clay minerals (Newman 1987). Minerals are divided on the basis of layer type and charge. A generic formula is given for each group, in which Y and Z represent tetrahedral and octahedral cations respectively, and the layer charge given is based on this formula unit. Chlorites differ from smectites and vermiculites, the clay layer charge in chlorites being balanced by positively charged hydroxide sheets located between the clay layers.

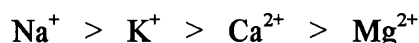
3.2.2 The Interlayer Region

The size of the interlayer space is regular throughout any particular clay. The clay layer spacing is defined as the repeat distance along the c^* or clay stacking axis and is denoted by d . It is therefore not the same as the separation between the clay layers as it includes the thickness of the clay layer itself. The clay layer spacing depends on both the clay type and the counterion, the effect of the counterion being illustrated in table 3.2.

Counterion	Clay Layer spacing / Å
Mg ²⁺	14.3
Ca ²⁺	15.1
Ba ²⁺	12.6
H ⁺	14.3
Li ⁺	12.6
Na ⁺	12.6
K ⁺	10.4

Table 3.2. Clay layer spacings of Macon County vermiculite as a function of counterion (Giesecking 1975)

Unlike cations within the clay layers the counterions are relatively mobile and in many cases will exchange rapidly with cations in a solution placed in contact with the clay. For example, in Llano vermiculite the predominant naturally occurring counterion is Mg²⁺; this clay would be called magnesium Llano (or Mg Llano). Sodium Llano could be prepared by soaking the clay crystals in an aqueous solution of NaCl, repeatedly replacing the solution until all Mg²⁺ ions had been removed. This procedure can also be used to determine the layer charge of a clay, by using infrared absorption spectroscopy to measure the number of ions which can be displaced from a sample. This gives the cation exchange capacity (CEC), which is usually expressed in milli-equivalents per gram of clay (1 meqg⁻¹ = 96.5Cg⁻¹). The CEC can however be higher than the surface charge of the clay due to the presence of excess ion pairs in the clay (Newman 1987). The CEC can also be affected by the mobility of the interlayer cations, which depends on both the cation and the clay type and charge. For example in mica the interlayer K⁺ ions are firmly bound because they sit in the hexagonal cavities on the clay surfaces. As a generalisation however the ease of substitution decreases along the series (Moore and Reynolds 1989):



3.2.3 Crystalline Swelling

In smectites and vermiculites, collectively referred to as swelling clays, the interlayer space can absorb water and other polar solvents, depending on the clay type and the counterion. This causes expansion of the clay along the stacking axis in a series of discrete steps, this process being called crystalline swelling (Kittrick 1969). Solvent absorption is driven by the solvation of both the counterions and the clay surfaces, and opposed by the counterion-clay Coulombic interactions: a model which assumes these to be independent has been shown to give qualitatively correct predictions for the hydration of alkali metal vermiculites (Kittrick 1969).

A wide variety of organic molecules can be absorbed into the interlayer region. Polar organic solvents such as methanol, ethanol and ethylene glycol can solvate the counterions. Ionic organic species such as alkyl-ammonium ions (RNH_3^+) can be exchanged into clay minerals as the counterion, giving a hydrophobic character to the interlayer. These organically treated clays can exhibit highly enhanced (10-30x) absorption of organic molecules such as benzene (Boyd et al 1988) or alcohols (Malberg et al 1989).

3.2.4 Importance and Uses of Clay Minerals

Clays are of vast importance, both in the environment and in industry (Velde 1992). Oil formation and migration occurs in buried clays (North 1990) and they are the site of many important transformations including the diagenetic reactions which are a major source of water in the earth's crust (Grim 1962). They are an important component of soils where they determine the transfer of water and dissolved species, for example from rainwater to groundwater (Velde 1992).

Due to their charged surfaces clays have been widely used to catalyse organic reactions. Reactions such as petroleum cracking occur on the external surfaces of clays which, being negatively charged, act as electron donors. Molecular conversion reactions such as hydrogenation can occur on the internal surfaces of clays when organic molecules are absorbed into the clay. The absorbent properties of clays are also useful in controlling pollution. Clays with a high CEC can be used to trap radioactive and / or poisonous heavy metal ions, which tend to bind strongly to the clay surfaces. They are therefore used for lining landfill sites and in radioactive waste containment. Organically treated clays can be used to absorb organic pollutants and air blown vermiculite is used for packaging chemicals, again because of their absorbent properties. Smectites are used in ceramics, for coating glossy papers and in oil drilling fluids. Understanding clay-fluid interactions is also crucial to ensure wellbore stability during oil extraction (Bailey et al 1991).

3.3 Interlayer Structure in Swelling Clays

The behaviour of swelling clay minerals is determined by the structure and dynamics of the interlayer region. This section summarises some of the previous work in this area, describing the interlayer in terms of:

- The position and orientation of species in the interlayer relative to the clay surfaces, considered both perpendicular to and parallel to the surface
- Interactions of interlayer species with the clay surfaces and with each other

3.3.1 Water in The Interlayer

Crystalline swelling of vermiculites in water occurs in a series of discrete steps, and there is much evidence, examples being given below, to indicate the existence of interlayer water in discrete layers parallel to the clay surfaces. This situation has been described as water molecules forming 'dielectric links' between the counterions and the surface oxygen atoms (Farmer and Russell 1971). X-ray diffraction experiments on Mg vermiculite have shown that two layers of water octahedrally co-ordinate the counterions, which are located in the mid-plane of the interlayer region. This structure can also be visualised as two layers of hexagonally close packed water molecules with Mg^{2+} ions in the octahedral sites (Mathieson 1958, Mathieson and Walker 1954, Shirozu and Bailey 1966). It was observed however that in Ba vermiculites the water molecules sit midway between the clay layers, the counterions being located either side of this plane (Telleria et al 1977).

Neutron diffraction in conjunction with isotope substitution has been used to study the water structure perpendicular to the clay surface in Na, Ca, Ni and Li Llano vermiculites (Skipper et al 1990, 1991, 1994 and 1995). The water was found in all cases

to exist in well ordered layers, the precise structure being strongly influenced by the counterion. The counterions were found to be located in the mid-plane of the interlayer space in all of these vermiculites. In Ni, Ca and Li vermiculites the counterions are octahedrally coordinated by six water molecules. With Ni and Li these octahedral $M(H_2O)_6^{z+}$ complexes are orientated so that the water molecules sit in two layers parallel to the clay surfaces. One O-H bond of each water molecule is orientated to hydrogen bond to the charge sites on the clay surfaces. With Ca the complexes are orientated with the water in three layers of two molecules each, four of the water molecules being hydrogen bonded to the clay surfaces. In Ni vermiculite water molecules are also absorbed onto the clay, sitting in the hexagonal cavities in the surface. The Na vermiculite was studied in a di- and mono-hydrate state. The dihydrate has a similar structure to that of Ni vermiculite but is less strongly structured, reflecting the weaker hydration of the Na^+ ion. In the mono-hydrate (formed at 30% relative humidity) the Na^+ ions are found to be in direct contact with the clay surfaces. This comparison of the hydration of Li^+ and Na^+ is consistent with the SERS studies of these ions at electrode surfaces described in chapter 2 (Zou et al 1997). Co vermiculite has also been studied (Adams and Riekel 1980) by neutron diffraction and again the water is found to sit in two layers, forming a complete first hydration shell around the ions.

Studies of the layer spacings in smectites also indicate layering of water molecules. For example, a Na smectite has four observed layer spacings (Moore and Hower 1986) as a function of relative humidity: 9.6, 12.4, 15.2 and 18.0 Å, representing transitions (with increasing humidity) from the dehydrated clay to 1, 2 and 3 layers of water molecules. At intermediate humidities ordered interstratification of two hydrate phases was also observed. Simulations have also provided evidence of up to four layers of water molecules in Na montmorillonite (Delville 1992). Density profiles fitted to

neutron diffraction data from a Na montmorillonite however suggest that this layering is less pronounced than in vermiculites (Hawkins and Egelstaff 1980).

Comparison of Cu smectites with Cu vermiculites has shown that the interlayer structure is dependant on the surface charge and structure - in the former $\text{Cu}(\text{H}_2\text{O})_6$ octahedra sit with the C_4 axis perpendicular to the clay surface while in the latter the complex is tilted at 45° , as in Ni and Li vermiculites (McBride et al 1975).

Various spectroscopic techniques have been used to investigate the dynamics of water molecules in the interlayer. NMR studies of Na smectites show that rotation of water molecules is slowed in the first one or two layers on the surface, but is unaffected beyond this (Woessner 1979). Similar results are obtained from inelastic neutron scattering studies of Li smectites (Poinsignon et al 1989). These also indicate that in addition to rotation of individual water molecules, rotation of the cation - water complexes occurs, with a correlation time of 30ps compared to 4-5ps for the individual molecules.

3.3.2 Organic Species in The Interlayer

Polar organic molecules can be absorbed and solvate the counterions in an analogous way to water, for example ethylene glycol forms a variety of one and two layer glycol complexes. Much work has been done (Lagaly 1976 for example) with organic molecules such as long chain alcohols and alkyl-ammonium ions. The structure of these systems has been interpreted (Walker 1967, Serratosa et al 1970) by considering the layer spacing to be determined by space constraints, the large size of the ions forcing them to lie essentially perpendicular to the clay layers.

With long chain ($n_c > 5$) alkyl-ammonium counterions the layer spacing in vermiculites is observed (Johns and Sen Gupta 1967) to increase linearly with the chain length. It is also observed that the layer spacing in butyl-, hexyl-, octyl-, decyl- and dodecyl-ammonium Llano vermiculites is reduced on drying at 65°C, for example the hexyl- system goes from $d = 28.1\text{\AA}$ to $d = 19.0\text{\AA}$. This is interpreted as due to increasing interpenetration of the alkyl chains as water is removed from the interlayer. The layer spacing in the 'collapsed' system is given by $d = 10.18 + 1.0n_c\text{\AA}$, where n_c is the number of carbon atoms in the alkyl chain. On the basis of this a model is proposed in which the alkyl chains form an angle of 55° with the clay layers, with the NH_3 groups adjacent to the clay surface and the C-N bond perpendicular to the surface (figure 3.4). The ions form one interpenetrating layer in the collapsed phases and two non-penetrating layers in the uncollapsed phase. X-ray diffraction was used to fit electron density profiles for the collapsed hexyl- and octyl-ammonium systems, confirming this model (Johns and Sen Gupta 1967). Infrared spectroscopy has confirmed that the NH_3 groups in octyl-ammonium vermiculites are hydrogen bonded to the clay surface, the nitrogen atoms being located at 4.8Å from the plane of the octahedral cations (Serratosa et al 1970).

Measurement of the layer spacing after treatment with n-alkyl-ammonium ions has become a standard method for estimating layer charge (Lagaly 1981), although inconsistencies can occur between different clays (Vali et al 1993). Neutron diffraction studies using isotope substitution on clays in which the counterion is the surfactant $\text{C}_{12}\text{H}_{25}\text{NMe}_3^+$ show that the alkyl chains again form an angle of 54° to the clay surface (Williams et al 1997).

For shorter alkyl chains and clays with a low layer charge (and so fewer counterions) it is suggested (Lagaly 1981) that the ions lie parallel to the clay surfaces in either one or two layers (figure 3.4).

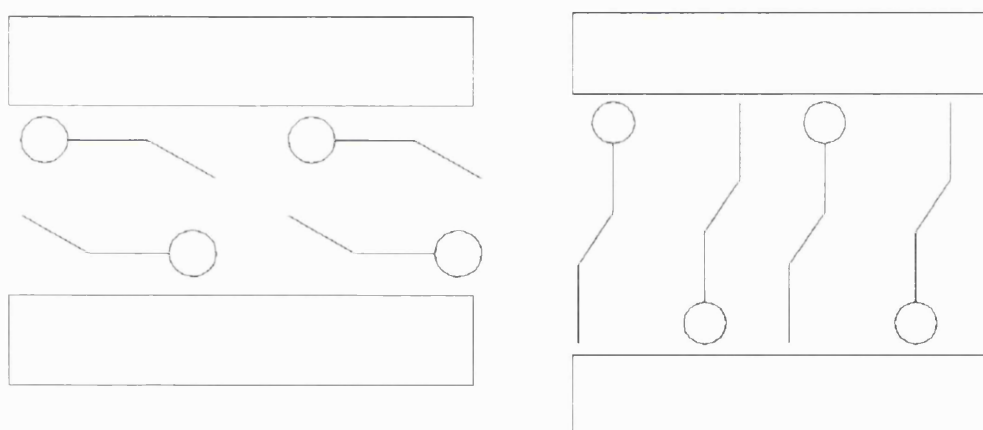


Figure 3.4. Schematic representation of alkyl-ammonium ions confined between clay layers, showing a possible transition in the ion arrangement as the alkyl chain is changed from ethyl to propyl and becomes too large to lie parallel to the clay surface. The arrangement shown in the right hand figure corresponds to the model in which the alkyl chains form an angle of 55° to the surface.

3.4 Macroscopic Swelling

Certain swelling clays will undergo macroscopic swelling when placed in water or a dilute solution of the counterion (Walker 1960 for example), absorbing many times their own volume of water to form a gel phase (figure 3.5). This is also referred to as colloidal or osmotic swelling. The solution added to induce macroscopic swelling in a clay will be referred to as the soaking (or swelling) solution; solution left in contact with a gel after swelling is complete will be referred to as the supernatant solution.

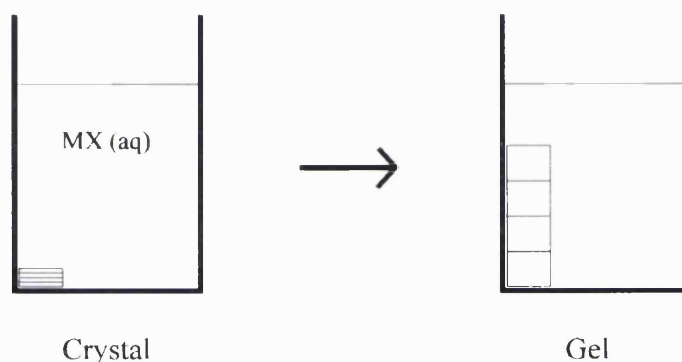


Figure 3.5. Schematic representation of macroscopic swelling of a vermiculite crystal in an aqueous solution to form a gel with a regular clay layer spacing.

The gels have been investigated using X-ray (Norrish 1954, Garrett and Walker 1962) and neutron diffraction (Braganza et al 1990) and have been found to have a regular clay layer spacing which can be as large as 600Å. If the sample is a vermiculite then a single coherent stack is formed, the externally observed expansion of the clay being commensurate with the increase in the layer spacing. The gels have no tendency to disperse into the surrounding solution.

Macroscopic swelling has been observed in the following systems:

i) n-butyl-ammonium ($\text{C}_4\text{H}_9\text{NH}_3^+$) vermiculites (Walker 1960). Swelling was also reported with n-propyl-ammonium ($\text{C}_3\text{H}_7\text{NH}_3^+$) and other branched alkyl-ammonium ions in which the main carbon chain is 3 or 4 carbons in length, for example isoamyl ($(\text{CH}_3)_2\text{CHC}_2\text{H}_4\text{NH}_3^+$).

ii) L-ornithine ($\text{CO}_2\text{HCHNH}_2\text{C}_3\text{H}_6\text{NH}_3^+$) (Rausell-Colom et al 1989, Gardner 1993) and L-lysine ($\text{CO}_2\text{HCHNH}_2\text{C}_2\text{H}_4\text{NH}_3^+$) vermiculites (Walker and Garrett 1961).

iii) Li^+ vermiculites (Walker and Milne 1950).

iv) Na^+ , Li^+ and Na^+ smectites (Norrish 1954)

It has been postulated from neutron diffraction studies of Li vermiculite (Skipper et al 1995) that dissociation of the counterions from the clay surfaces is a necessary precursor to macroscopic swelling. Infrared spectroscopic studies of swelling Na montmorillonite also show that the counterions readily become hydrated (Sposito et al 1983). The interlayer structure in the crystalline phase of the swelling alkyl-ammonium vermiculites has not however been previously determined.

Comparable swelling behaviour can also occur when clays containing long chain alkyl-ammonium counterions are immersed in organic liquids. For example alkyl-ammonium bentonites in which the alkyl chain length is >7 will swell in nitrobenzene (Jordan 1948).

3.4.1 Variables Affecting Macroscopic Swelling Behaviour

The summary which follows refers principally to BuNH₃ vermiculite swelling, this system having been extensively studied. Differences in the behaviour of the other clays which exhibit macroscopic swelling are noted where necessary. The principle variables which affect the swelling process are:

I) The salt concentration in the soaking solution (c). The layer spacing in the BuNH₃ vermiculite gels decreases with increasing salt concentration (figure 3.6a), being proportional to $c^{-1/2}$ (Crawford et al 1991). The gels therefore behave as classical one-dimensional colloids (Hunter 1993). There is a certain maximum concentration above which macroscopic swelling will not occur. For BuNH₃ vermiculite at 4°C the transition to non-swelling behaviour occurs at ~0.2M, the layer spacing at this concentration being ~80Å compared to the crystal layer spacing of 19.4Å. As a result of this, layer spacings between 19.4Å and ~80Å cannot be obtained by controlling the salt concentration. The maximum layer spacing obtainable is limited by the difficulty of preparing gels in very dilute solutions; at a concentration of 0.001M the layer spacing is ~600Å. Smectites and Li vermiculites also show the same qualitative d vs $c^{-1/2}$ swelling dependence. The layer spacings in swollen smectites are lower than in the vermiculites however, and unlike the vermiculites the transition is not fully reversible, possibly due to face-edge interactions between the clay particles (Norrish and Rausell-Colom 1963). In the Li vermiculite gels the layer spacing is less well characterised. Individual crystals also more frequently fail to swell than do those of BuNH₃ vermiculite (Norrish and Rausell-Colom 1963).

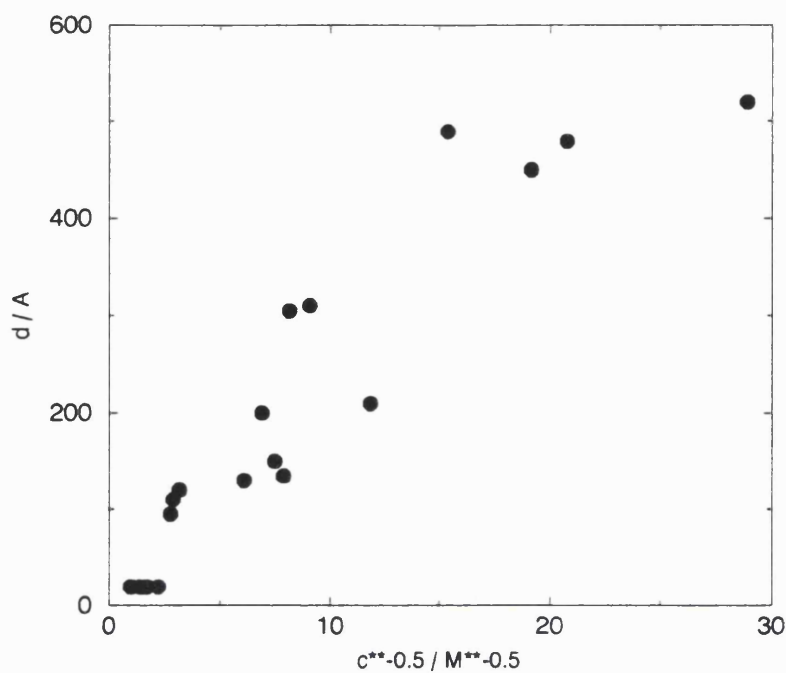


Fig 3.6a. Concentration dependence of butyl-ammonium vermiculite swelling, showing the layer spacing (d) at 277K as a function of salt concentration (c).

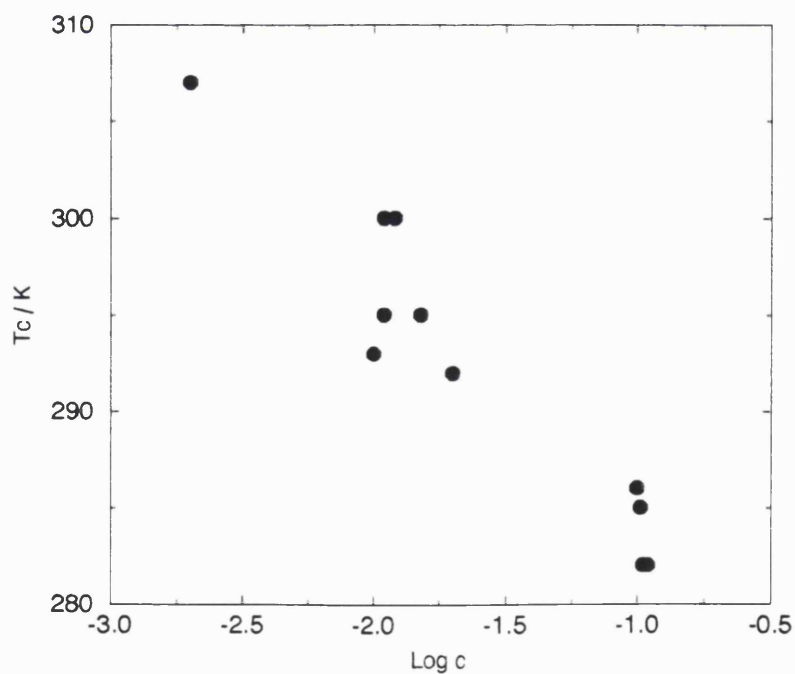


Fig 3.6b. Temperature dependence of butyl-ammonium vermiculite swelling, showing the temperature at which transition to the crystal phase occurs (T_c) as a function of salt concentration (c).

II) Temperature. The gels undergo a transition to the crystal phase above a specific transition temperature, T_c . For BuNH_3 vermiculite T_c is of the order of 300K and decreases proportionally to $\log c$ (Crawford et al 1991) (figure 3.7b). There is no evidence for the existence of this transition in smectites or Li vermiculites.

III) Volume fraction (r). The layer spacing in the gels increases as the volume fraction (defined as the ratio of volume of clay / total volume of clay plus solution) is decreased. The reason for this is twofold. Firstly, salt is always present in the clay crystals, either in the interlayer space or trapped in cracks and faults. Secondly, salt is excluded from the solution absorbed into the gel due to the additional ionic strength of the clay layer charge plus counterions, so the actual salt concentration in the supernatant solution is increased. Both these effects become greater as the volume fraction of clay is increased. The amount of salt trapped in BuNH_3 vermiculite has been measured and was found even after 20 washes in H_2O at 80°C to be 0.10 ± 0.05 moles per litre of clay (Williams et al 1994).

IV) Pressure. Hydrostatic pressure has been applied to BuNH_3 vermiculite crystals in contact with an aqueous solution, and is observed to induce swelling at temperatures above T_c (Smalley et al 1989). This indicates a reduction in the total volume when macroscopic swelling takes place (section 3.4.2).

V) Uniaxial stress (p_{uniaxial}). Work has been done (Crawford et al 1991) using quartz levers to apply uniaxial pressure along the swelling axis of the clay, investigating layer spacings between $100\text{\AA}$ and $400\text{\AA}$. The layer spacing was measured as a function of uniaxial pressure and found to decrease linearly in proportion to $\log p_{\text{uniaxial}}$. This is

consistent with the predictions of the DLVO and Sogami theories.

VI) **pH.** Clay behaviour can be altered by pH, due to the presence of hydroxyl groups on the clay surface. Ornithine and lysine are amino acids which can exist in a cationic or zwitterionic form depending on pH, and so the swelling of amino acid vermiculite complexes can be pH dependant (Gardner 1993).

3.4.2 Thermodynamics of The Swelling Transition

The transition between the crystal and gel phases is observed to be fully reversible at the microscopic level with respect to salt concentration, temperature and pressure (Smalley et al 1989), and so it is a true thermodynamic transition. Calorimetric measurements of the heat capacity and the pressure dependence of swelling have been used to calculate the enthalpy, entropy and volume changes associated with swelling of BuNH₃ vermiculite gels (Smalley et al 1989). For a gel in 0.1M BuNH₃Cl (aq) at 10°C with a layer spacing of ~100Å the enthalpy, entropy and volume changes associated with the swelling process are

$$\Delta H = -5.2 \pm 0.1 \text{ J per gram of clay}$$

$$\Delta S = -0.0183 \pm 0.0004 \text{ J/K per gram of clay}$$

$$\Delta V = -0.0215 \text{ cm}^3 \text{ per gram of clay}$$

The swelling process is therefore entropically unfavourable, and is accompanied by a slight decrease in the total volume of the system. This change corresponds to an increase of the density of water in the interlayer space of ~ 0.1% compared to bulk water.

3.5 Measuring The Electrical Double Layer Structure in Macroscopically Swollen Vermiculite Gels

Macroscopically swollen alkyl-ammonium vermiculite gels have many inherent advantages for the study of liquids at surfaces. The gels contain large internal surfaces, so that a significant proportion of any sample is comprised of solid-liquid interfaces, an advantage in any experimental technique (such as diffraction) which is intensity limited. Furthermore these surfaces are well characterised, being flat at both macroscopic (cm) and atomic ($\text{\AA}$) length scales.

The layer spacing in the gels is sufficiently regular to allow diffraction studies which treat the gel as a crystal. Because vermiculites occur as macroscopic (fully orientated) crystals the gels can be aligned to investigate the liquid structure solely in one dimension, usually perpendicular to the clay layers. This reduction from a three to a one-dimensional problem assists greatly in interpreting the structure of a complex, multi-component system such as the solid-liquid interface.

The swelling behaviour of PrNH_3 vermiculite was investigated (chapter 6) and it was found that gels prepared in 0.5M solutions have a layer spacing of $\sim 40\text{\AA}$, a spacing much smaller than any that can easily be obtained in BuNH_3 gels. This layer spacing is sufficiently large to allow an electrical double layer structure to develop (Israelachvili and Pashley 1983, Rose and Benjamin 1991, Toney et al 1995), but is also sufficiently small to measure conveniently by diffraction (chapter 4).

It was also found (chapter 6) that, like the BuNH_3 gels, the PrNH_3 gels act as classical colloids, exhibiting a layer spacing which is inversely proportional to the square root of the salt concentration in the soaking solution. This is in agreement with predictions of the behaviour of colloidal systems made by primitive model based theories such as the DLVO (Derjaguin and Landau 1941, Verwey and Overbeek 1948) and

Sogami (Sogami and Ise 1984) theories. The vermiculite gels are therefore an ideal system to test the assumptions which the primitive model makes about the electrical double layer structure.

The alkyl-ammonium ions behave almost ideally in solution. Studies of the partial molar volumes of these ions in a solution of D₂O have shown (Desnoyers and Arel 1967) that at concentrations up to 1M aggregation does not occur with any alkyl-ammonium ion in which the alkyl chain length is <7 carbon atoms. Their enthalpies of solvation have also been measured (Krishnan and Friedman 1970). These are all found to be small (<10kJ/mol) and show no systematic trend, and of the two ions which induce macroscopic swelling BuNH₃⁺ has a negative and PrNH₃⁺ a positive enthalpy of solvation.

A disadvantage of using vermiculite gels is that there is almost inevitably some uncertainty in their composition, caused by the continuous variety which is possible in clay minerals. Even clays of the same type can contain different proportions of layer cations, and progressive alteration of the layers can occur. For example, Fe(III) is sometimes observed leeching into the soaking solution of iron rich vermiculites such as Eucatex, this occurring over several months. The layer charge is estimated by the CEC, which can give a degree of underestimation depending on the ease of exchange of the counterions. Finally there can be a large degree of error (up to ~10%) in measurements such as those shown in fig 3.6a due to uncertainty in the salt concentration caused by salt trapped in the clay.

NEUTRON DIFFRACTION

4.1 Contents

This chapter covers the theory of the scattering of radiation from condensed matter and its application to studies of molecular structure. An introduction including general definitions is given in sections 4.2 and 4.3. The method of time-of-flight neutron diffraction is then outlined, including data correction procedures. For a more detailed treatment of the theory of neutron diffraction see *Theory of Neutron Scattering from Condensed Matter* (Lovesey 1978) and *Introduction to the theory of Thermal Neutron Scattering* (Squires 1978).

4.2 Scattering of Radiation From Matter

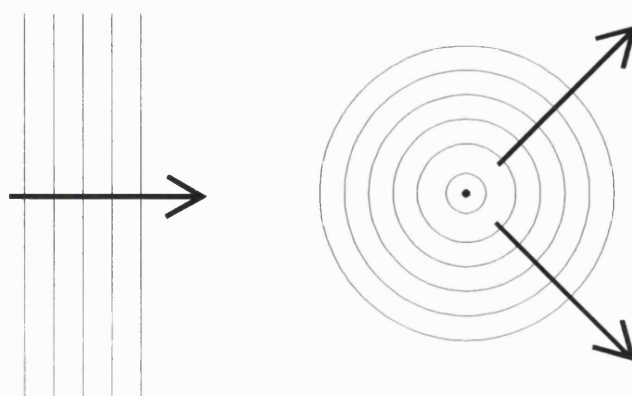


Figure 4.1. Representation of an incoming beam as a plane wave and a scattered beam as a spherical wave, assuming that the target is much smaller than the wavelength of the radiation.

If we consider the general case of an incoming beam of radiation scattering from a target such as a nucleus we can represent the incoming radiation by a plane wavefunction. If we assume i) that the target is much smaller than the wavelength of the radiation, and ii) that there is no energy transfer to the target, then the scattered radiation can be described as a spherical wavefunction (figure 4.1). This is the Born approximation. We can then write the wavefunctions for the incoming and scattered beams

$$\psi_{in} = \exp(ik_0 z) \quad (4.1a)$$

$$\psi_{scat} = \frac{-b}{r} \exp(ik_0 r) \quad (4.1b)$$

where k_0 is the magnitude of the wave vector $\mathbf{k}$, z is the position of the incoming wave on an axis in the direction of $\mathbf{k}$, r is the distance from the target of the scattered wave at position $\mathbf{r}$, and b is a constant related to the strength of the interaction causing the scattering process (the scattering length).

A scattering event can also be characterised by a momentum transfer (or scattering) vector, $\mathbf{Q}$, and an energy transfer, $\hbar \omega$, given respectively by:

$$\hbar \mathbf{Q} = \hbar \mathbf{k}_0 - \hbar \mathbf{k} \quad (4.2a)$$

$$\hbar \omega = E_0 - E \quad (4.2b)$$

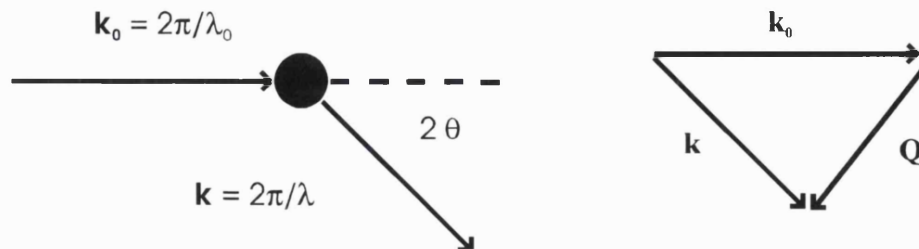


Figure 4.2. a) Geometry of a scattering event in which a quantum with initial wavelength λ_0 and momentum $\mathbf{k}_0$ is scattered through an angle 2θ and has a final wavelength λ and momentum $\mathbf{k}$. b) Vector diagram showing the momentum transfer vector, $\mathbf{Q}$, associated with this scattering event.

Scattering events in which there is no energy transfer between the scattered quantum and the target (where $E=E_0$ and so $|\mathbf{k}| = |\mathbf{k}_0|$) are referred to as elastic scattering; those where there is an energy transfer ($E \neq E_0$) as inelastic. The momentum transfer vector is also called the scattering vector. The angle between the initial and final momentum vectors will be denoted as 2θ , θ being called the scattering angle.

4.2.1 The Differential Cross Section

In a scattering experiment we use a detector to measure the number of quanta scattered from a sample as a function of the scattering angle and the energy of the scattered quanta. This is the double differential cross section (DDCS) which we define per atom per unit flux as

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{Number of quanta scattered in a small solid angle } d\Omega \text{ at angle } 2\theta \text{ with final energy between } E' \text{ and } E'+dE'}{\text{incident flux, } \Phi \times \text{number of atoms, } N \times d\Omega \times dE} \quad (4.3)$$

In a diffraction experiment the energy of the scattered quanta is not analysed, so we are measuring the integral of equation 4.3. This is the differential cross section (DCS)

$$\frac{d\sigma}{d\Omega} = \frac{\text{Number of quanta scattered in a small solid angle } d\Omega \text{ at angle } 2\theta}{\Phi \times N \times d\Omega} \quad (4.4)$$

The integral of the DCS over all angles gives σ_{total} , the total scattering cross section per atom:

$$\sigma_{total} = \frac{\text{Total number of quanta scattered in all directions}}{\Phi \times N} \quad (4.5)$$

which is related to the scattering length by

$$\sigma_{total} = 4\pi b^2 \quad (4.6)$$

4.2.2 The Total Structure Factor

Assuming that there are no corrections to be applied to the data then the DDCS is equal to the total structure factor, $F(Q, \omega)$, where Q is the magnitude of the momentum transfer vector (which is often referred to simply as the momentum transfer). The function $F(Q, \omega)$ is made up of the sum of all scattering processes occurring in the sample. If we were able to obtain $F(Q, \omega)$ over all possible magnitudes of momentum and energy transfers it would contain all the structural and dynamical information for the sample in the momentum and energy transfers respectively. Any real experiment however can only measure $F(Q, \omega)$ over a limited range, depending on the constraints of a particular instrument.

In a diffraction experiment we investigate the structure rather than the dynamics of the sample and so wish to obtain $F(Q, 0)$. The data is analysed only as a function of Q and it is assumed that all scattering is elastic, i.e. that the measured $F(Q, \omega)$ is equal to $F(Q, 0)$, which will also be written from here as $F(Q)$. This is the Static Approximation. In practice energy transfer often occurs during scattering from a nucleus due to nuclear recoil, especially when the scattered quantum is of comparable mass to the target nucleus (for example a neutron scattering from a hydrogen nucleus). As a result of this assumption an inelastic correction is sometimes needed to obtain $F(Q)$ from the DCS.

4.2.3 Coherent and Incoherent Scattering

Although we can define the total scattering from a single atom by its scattering length, when we consider the scattering from many atoms of the same type we have to consider deviations from the average scattering length. The total scattering can be divided into two components. The first is the scattering that results from the average

scattering length of the targets. This contains the structural information on the sample (section 4.3 below) and is referred to as coherent scattering. The second is the scattering resulting from random fluctuations in the scattering length of individual targets. This is the incoherent scattering, which cannot contain structural information as it arises from a random distribution. Fluctuations in the neutron scattering length of a nucleus can arise from the random distribution of isotopes and/or nuclear spins within a sample. We can define coherent and incoherent neutron scattering lengths for a species

$$b_{coh}^2 = \bar{b}^2 \quad (4.7a)$$

$$b_{inc}^2 = \overline{b^2} - \bar{b}^2 \quad (4.7b)$$

Because the incoherent scattering is independent of structure it is given simply by a summation over each species present in a sample. We can write the total structure factor as the coherent scattering, denoted by $I(Q)$, plus the incoherent scattering

$$F(Q) = I(Q) + \sum_{\alpha} c_{\alpha} b_{\alpha, inc}^2 \quad (4.8)$$

where c_{α} is the atomic fraction of species α which has an incoherent scattering length $b_{\alpha, inc}$. Note that the incoherent scattering is independent of Q , and so in an experiment can be easily subtracted from $F(Q)$ to obtain $I(Q)$.

4.2.4 Note on Terminology

The coherent scattering is related to the structure of a sample but there are several definitions to describe it (section 4.3). Unfortunately this leads to ambiguities. With amorphous samples it is common to refer to the coherent scattering as the structure factor, while in crystallography the structure factor is defined as a quantity of which the modulus squared is the coherent scattering. This confusion is further compounded by the use of the same symbols to denote different quantities. For the purposes of this thesis the term ‘structure factor’ refers to the crystallographic definition which will be given in equation 4.12; this will be abbreviated as $S(Q)$. $F(Q)$ will denote the total structure factor and $I(Q)$ will denote the coherent scattering. Other non-standard notations will be introduced as required.

4.3 Interference and Coherent Scattering

4.3.1 The Bragg Condition

To calculate the form of the coherent scattering from an assembly of more than one atom, we go back to the Born Approximation (section 4.2), treating the scattered quanta as spherical waves.

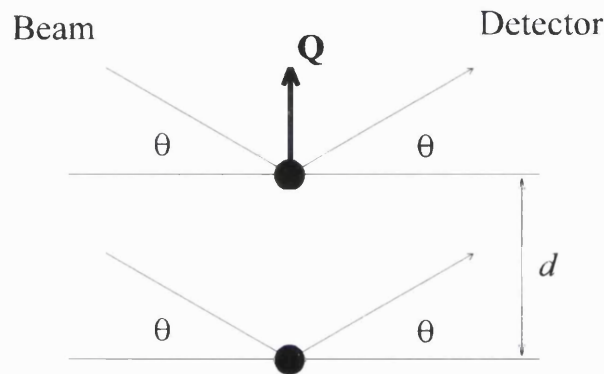


Figure 4.3. Geometry of scattering of an incident beam by two planes of atoms separated by a distance d , with the momentum transfer vector perpendicular to the planes of atoms.

We can define a phase relationship for scattered quanta. Consider two planes of atoms scattering a beam of quanta with wavelength λ through an angle 2θ , with a separation d along an axis parallel to the momentum transfer vector (figure 4.3). For totally constructive interference to occur the path difference for the two scattered beams must equal an integral number of wavelengths (the Bragg condition):

$$2d \sin \theta = n\lambda \quad (4.9)$$

It is more useful to express the Bragg condition as a function of Q than by having to define both θ and λ . From equations 4.2a and 4.9 it follows that, assuming elastic scattering, the Bragg condition is satisfied when

$$Q = 2|k_0| \sin \theta = \frac{4\pi \sin \theta}{\lambda} \quad (4.10)$$

Combining equations 4.9 and 4.10 gives the useful relationship (assuming $n = 1$)

$$Q = \frac{2\pi}{d} \quad (4.11)$$

Having related the scattering from two atoms to their separation along the axis of the scattering vector we can define the total coherent scattering from the separation of every pair of atoms in a sample.

4.3.2 Definition of The Coherent Scattering From a Crystal

In a crystalline material, if the Bragg condition is satisfied for equivalent atoms in adjacent unit cells, then it must also be satisfied by the equivalent atom in every other unit cell, and constructive interference results. If it is not satisfied, even by a very small fraction, then completely destructive interference will result: assuming that there are a large number of unit cells then for every atom there will always be an atom positioned to scatter completely out of phase with the first. Coherent scattering therefore only occurs in a series of sharp peaks (the Bragg reflections). These will be seen at regular intervals in Q space corresponding (equation 4.11) in real space to the separation of planes of atoms within the unit cell. Peaks are denoted by (hkl) where h , k and l are the Miller indices which give the orders with respect to each axis of the unit cell.

The intensity of each Bragg reflection is dependant on the phase relationship of all the atoms in the unit cell, which in turn depends on their position along the axis of the cell parallel to Q . The summation of the wavefunctions for scattering from all atoms in the unit cell is given by (from equation 4.1b)

$$S(Q) = \sum_n b_n e^{iQz_n} \quad (4.12)$$

where b_n is the scattering length of atom n , z_n is the atom's position an axis parallel to Q and $S(Q)$ is called the structure factor. Expanding the exponential term gives

$$S(Q) = \sum_n b_n \cos(Qz_n) + i \sum_n b_n \sin(Qz_n) \quad (4.13)$$

We can also express this as an integral over the length of the unit cell

$$S(Q) = \int_0^d \rho(z) (\cos(Qz) + i \sin(Qz)) dz \quad (4.14)$$

where z is the position in a unit cell of length d and $\rho(z)$ is the scattering density profile.

If the unit cell has a centre of symmetry, which is generally the case for clay minerals, then the sine term must equal zero. This is because the sine term is anti-symmetric, so the integral of this term over the first and second halves of the unit cell will have the same magnitude but opposite signs. In this special case equation 4.14 simplifies to

$$S(Q) = \int_0^d \rho(z) \cos(Qz) dz \quad (4.15)$$

This relationship between the scattering density profile and the structure factor is illustrated in figure 4.4 and the accompanying text. The coherent scattering, which is also called the Bragg intensity, is the amplitude of this wave

$$I(Q) = S^*(Q) S(Q) \quad (4.16)$$

From equation 4.16 it follows that the observed coherent scattering must always be positive. As a result of this we can never observe the sign of the structure factor. Furthermore, because constructive interference only occurs at the Bragg reflections we can only observe the magnitude of the structure factor at values of Q for which the Bragg condition is satisfied. Because of this loss of information it is not possible to calculate a scattering density profile directly from the coherent scattering and so a fitting procedure is required. The fitting procedure used for the experiments described in this thesis is described in chapter 5.

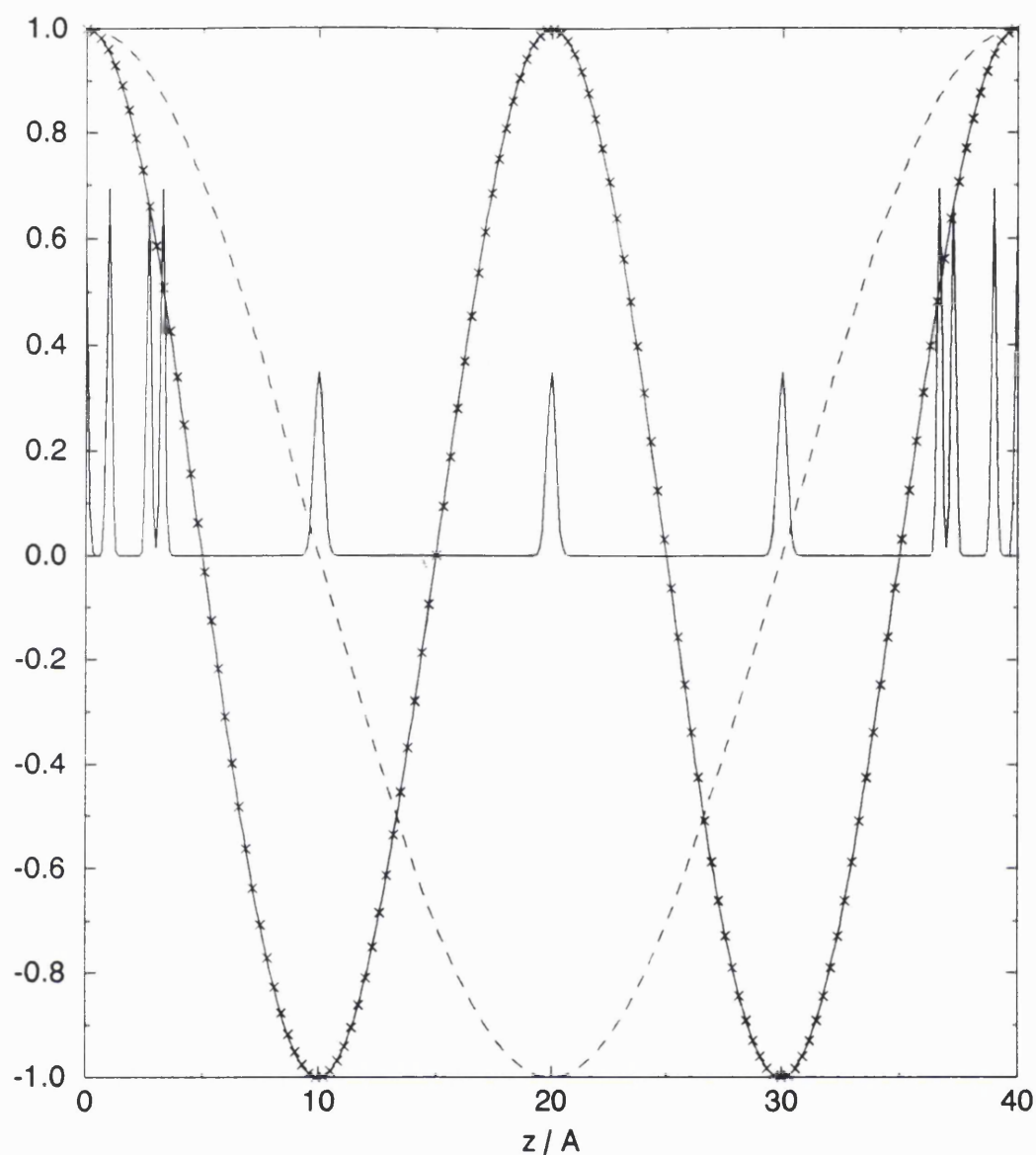


Figure 4.4. Plot of the scattering density profile (solid line; arbitrary units on the y axis) along the c^* axis for a hypothetical clay gel with a layer spacing of $40\text{\AA}$. Peaks near $z = 0$ and $z = 40\text{\AA}$ represent atoms in the clay layers; peaks at $10, 20$ and $30\text{\AA}$ represent three possible positions of an atom in the interlayer. The function $\cos(Qz)$ is shown for Q values corresponding to the (001) (dashed line) and (002) Bragg reflections (solid line with crosses). $S(Q)$ at a Bragg reflection is given by a summation over the density profile weighted by the appropriate function. Atoms in the centre of the cell will therefore make a negative contribution to the (001) and a positive one to the (002). Atoms at one quarter and three quarters of the unit cell length however will make no contribution to (001) and a negative contribution to the (002). It is therefore possible to locate species in the interlayer from the changes in Bragg intensities accompanying a change of the scattering profile. In neutron diffraction this is achieved by isotope substitution.

We have so far treated the atomic separation in only one dimension, that parallel to the scattering vector (figure 4.3). It is therefore important to consider what this dimension represents for different materials. In the case of a single crystal the distribution of atoms on the z axis is dependant on the orientation of the sample with respect to $\mathbf{Q}$. Different orientations of the crystal can therefore lead to diffraction from different sets of planes of atoms in the crystal. In a crystal where one axis of the unit cell is orthogonal to the others it is possible to align the sample with this axis parallel to $\mathbf{Q}$ and so investigate the structure solely along that axis. In the case of clays this means that they can be aligned to study the structure perpendicular to the clay surface (along the c^* axis). This is an important advantage as it greatly simplifies the analysis of a complex, multicomponent system. It does involve the loss of information on the structure parallel to the surface, but as the structure developed in the electrical double layer is expected to be manifested principally along the c^* axis this is not so important.

In a powder or a liquid or amorphous sample there is no long range orientational order and whatever the relative orientation of beam, sample and detector we investigate the structure in all three (equivalent) dimensions simultaneously.

4.3.3 Definition of The Coherent Scattering From a Liquid

Although the vermiculites studied in this thesis are treated as crystals, it is useful to introduce some definitions for diffraction from liquids. The definition of the structure factor for a crystal represents the special case where we can consider the phase relationship of each scattered wave with respect to a fixed reference point. In a liquid there is no such reference point and so we make a universally valid definition of $I(\mathbf{Q})$ as a double summation over every pair of atoms in the entire sample.

This however introduces a distinction between two types of coherent scattering. The self (or single atom) scattering results from terms summing over the same atom, the distinct (or interference) scattering from all the terms summing over different atoms. For the purposes of this thesis these will be abbreviated as $C(Q)$ and $D(Q)$ respectively. The distinction is necessary because summation over an identical atom cannot give structural information. The self scattering is therefore independent of Q and is given by a summation over all atoms species in the sample

$$C(Q) = \sum_{\alpha} c_{\alpha} \overline{b_{\alpha,coh}^2} \quad (4.18)$$

where c_{α} is the mole fraction and $b_{\alpha,coh}$ the coherent scattering length of species α . It should be noted that although this definition is very similar to that of the incoherent scattering (equation 4.8) the self scattering is still coherent scattering, although it cannot contain structural information. This is contained in the distinct scattering, which can be described in terms of the pair distribution function, $g(r)$. This gives the number of atoms at position r given an atom at the origin, averaging over all atoms in the sample

$$D(Q) = \rho \int (g(r) - 1) e^{iQr} dr \quad (4.19)$$

where ρ is the number density of atoms in the sample, which the pair distribution function tends to as $|r|$ becomes large. Note therefore that, unlike Bragg intensities, the distinct scattering oscillates about zero: the self scattering represents the coherent scattering which would be observed if there was no structure, while the distinct scattering contributes an oscillatory component around the self scattering level.

In a liquid there is no long range orientational order and so we can probe the entire structure in one dimension, all dimensions being equivalent. As a result $g(r)$ depends only on the magnitude of r and equation 4.19 can be simplified to

$$D(Q) = 1 + \frac{4\pi\rho}{Q} \int_0^\infty (g(r) - 1) \sin(Qr) \quad (4.20)$$

In a multicomponent system the distinct scattering is given by a sum over the distinct scattering from each pair of atoms, $D_{\alpha\beta}(Q)$, weighted by the scattering lengths for atoms of type α and β . These are related by equation 4.20 to the partial distribution functions $g_{\alpha\beta}(r)$ describing the distribution of those species. The total structure factor is therefore given by (incoherent scattering plus self and distinct terms)

$$F(Q) = \sum_{\alpha} c_{\alpha} \overline{b_{\alpha,inc}^2} + \sum_{\alpha} c_{\alpha} \overline{b_{\alpha,coh}^2} + \sum_{\alpha,\beta} c_{\alpha} \overline{b_{\alpha,coh}} c_{\beta} \overline{b_{\beta,coh}} (D_{\alpha\beta}(Q) - 1) \quad (4.21)$$

4.3.4 Disorder in Crystals

The definition of the structure factor used in equation 4.14 is a summation over a precisely repeating array of atoms, which is not the case except for a perfectly crystalline material at 0K. In reality random deviations from the perfect crystal structure will occur, both due to defects in the lattice and the thermal motion of the atoms. The observed scattering arises from a distribution averaged over the whole sample volume and over the time of the experiment. These factors reduce and broaden the Bragg peaks as the Bragg condition is met by different parts of the sample over a range of momentum transfers.

In a clay mineral there are several factors to be considered. The mosaicity is the degree of tilting of individual crystal blocks that make up a clay mineral, the mosaic spread of a vermiculite being typically $\pm 5^\circ$ (Crawford et al 1991) and that of a smectite $\pm 10 - 20^\circ$. The dispersivity of a sample is the average deviation in the clay layer spacing. This is expected to be greater in a macroscopically swollen clay gel than in a clay crystal

because of the larger layer spacing. We can take account of these factors, as well as the thermal disorder, by incorporating a mosaic factor, $M(Q)$, into equation 4.16.

$$I(Q) = S^*(Q) S(Q) M(Q) \quad (4.22)$$

The actual $M(Q)$ used in the experiments described in this thesis is a Lorentzian. This can be derived by treating the clay plates as disk shaped crystallites and assuming that the angle between the clay plates and the c^* axis, α , is sufficiently small that $\sin \alpha \approx \alpha$ and $\cos \alpha \approx 1$ (Skipper et al 1990).

4.3.5 Long versus Short Range Ordering in Clay Gels

In the case of a clay gel there is a second, more subtle consideration. It is desirable to treat a clay gel as a crystal in order to obtain the absolute positions of species in the interlayer with reference to the clay layers. The clay layers and any structure developed in the electrical double layer are regularly repeated and so can be defined by a repeating unit cell. However, the structure in the centre of the interlayer region may well be liquid in nature: this region will contain short range correlations between water molecules which have no fixed position relative to the clay layers, and so cannot be described by a unit cell.

Unlike random deviations from a crystal structure this additional short range order will give rise to coherent scattering, so it must be included in any description of the system. To summarise: we can get more information by describing a clay gel by a unit cell than we can describing it by a pair distribution function, but a single density profile cannot include liquid like correlations and so cannot adequately describe a clay gel.

In order to get round this problem it is necessary to describe the clay gel by a series of scattering density profiles, each of which can contain short range correlations. Taking the average of these gives the average scattering density profile in the unit cell, in which any oscillations must be due to long range ordering.

Finally, it should be noted that this distinction between long and short range order in clays should not be confused with referring to unswollen clays as crystals and swollen clays as gels. The crystal/gel nomenclature is given on the basis of the appearance of the samples and does not imply that the latter do not contain long range order.

4.4 Time-of-Flight Neutron Diffraction

Neutrons for diffraction experiments can be produced in two ways, either by spallation or from a reactor. The experiments described in this thesis were carried out using the ISIS Facility at the Rutherford-Appleton Laboratory, which is a spallation source. An accelerator ring is used to accelerate a proton beam which hits a Ta (or U) target, the protons breaking up the target nuclei (spallation), neutrons being released during this process. The proton beam is pulsed with a frequency of 50Hz, a pulse of neutrons lasting $\sim 1\mu\text{s}$ being produced by the target every 20ms. The neutrons released from the target have too short a wavelength to be useful for structural studies, so are slowed down by a moderator in which they lose energy in inelastic collisions with other nuclei, emerging with a range of wavelengths. A typical wavelength spectrum is shown in figure 4.5.

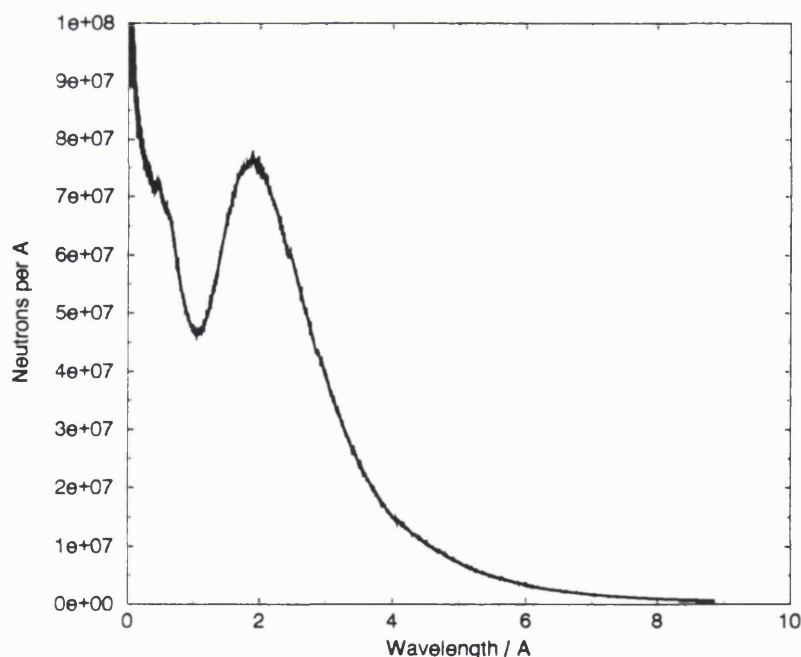


Figure 4.5. Neutron wavelength spectrum recorded by the incident beam monitor on the LAD Diffractometer. The spectrum consists of i) fast (low wavelength) neutrons, and ii) a broad distribution of wavelengths of neutrons which have been slowed by the moderator.

Using a pulsed neutron source allows a time-of-flight (ToF) measurement to be used. A ToF experiment takes advantage of the pulsed neutron source by recording both the scattering angle and time of arrival of detected neutrons. Assuming that the time spent in the moderator is negligible, then, knowing the distance from the target to the detector, the time of flight of the neutron can be related to its wavelength by the de Broglie relationship ($\lambda=h/p$, where p is the momentum of the neutron). The beam does not need monochromating and it is possible to measure simultaneously over a wide Q range, limited by the detector positions and the available wavelength range. This is an advantage in studying vermiculites as data is needed at sufficiently low Q to measure the (001) Bragg reflection. Data is also needed at high Q as this limits the real space resolution of an experiment, given (equation 4.11) by $2\pi/Q_{\max}$. A second advantage of the ToF experiment is that the beam-sample-detector geometry is fixed, which makes it easier to accurately correct data collected from irregularly shaped samples such as vermiculites.

The beam is defined using a collimator. This is usually constructed of a material containing boron, which has a high neutron capture cross section, to shield the neutron beam. The angular resolution of an experiment is limited by the degree of collimation of the beam; there is however a trade off as increasing the collimation usually reduces the beam intensity, and so an instrument must be designed to give a compromise depending on the samples being studied. The beam size at the sample is usually further defined using a beam mask. Two types of detector are used for neutrons, either gas ionisation (usually ^3He) or scintillation (usually ZnS). Scintillation detectors have a shorter dead time (4.6.7 below) but are more sensitive to background radiation. Two instruments were used for the experiments described in this thesis. These are described with the experimental procedures in chapters 5 and 6.

4.5 Neutron Scattering Lengths

An important feature of neutron scattering is that the variation in the coherent and incoherent scattering lengths of different nuclei is large and often irregular, even between isotopes. Scattering lengths of some common nuclei are listed in table 4.1 (Sears 1992).

Nucleus	$b_{coh} / 10^{-14} \text{ m}$	$b_{inc} / 10^{-14} \text{ m}$
^1H	-0.3374	2.527
^2H	0.6671	0.404
^{12}C	0.6651	0
^{14}N	0.644	0.20
^{15}N	0.937	-0.002
^{16}O	0.5805	0
^{24}Mg	0.566	0
^{27}Al	0.345	0.0256
^{28}Si	0.4107	0
^{48}Ti	-0.608	0
^{51}V	-0.03824	0.635
^{56}Fe	0.994	0
^{90}Zr	0.64	0

Table 4.1. Coherent and incoherent scattering lengths for nuclei of selected isotopes.

The variation in coherent scattering length between isotopes is a crucial advantage of neutron diffraction, as it allows the scattering density profile of a unit cell to be substantially altered by isotope substitution. By fitting to the resulting differences which are observed in the coherent scattering it is possible to locate the substituted species (figure 4.4). The most commonly used substitution is perhaps that of hydrogen/deuterium, as these have very different neutron scattering lengths (table 4.1). Furthermore, unlike X-rays, hydrogen scatters neutrons relatively strongly. For amorphous and/or many component systems the benefits of isotope substitution can be

decisive in identifying the structure, especially where several species can be individually substituted.

These methods assume that isotopic substitution does not alter the sample structure. Isotopes do have a measurable effect on bond lengths, for example in water vapour the O-H length is 0.9572Å while the O-D length 0.9575Å (Hobbs 1974). For n-alkyl-ammonium ions the enthalpies of transfer from H₂O to D₂O are non-zero, although small (<1kJmol⁻¹) (Krishnan and Friedman 1970). Monte Carlo simulations which include quantum effects have suggested that there should be an observable difference in the oxygen-oxygen distribution between D₂O and H₂O (Kuharsky and Rossky 1985) and there are observed differences in the physical properties of the two liquids (Lide 1995). Finally, the principle of the isotope effect on reaction rates is also well established in organic chemistry (Sykes 1986). These however are relatively small effects and it is generally accepted that isotope substitution does not significantly alter structure, especially as in most systems the number of substituted nuclei is much less than in the case of H₂O/D₂O.

The sign of the scattering length is also variable, opposite signs representing species which scatter neutrons 180° out of phase. The scattering length can also have an imaginary component, representing neutron capture processes (absorption). The variable phase of the scattering length is a useful property as it permits mixtures of two elements with an average coherent scattering length of zero, a highly desirable feature for sample containers whose scattering has to be subtracted from that from a sample. TiZr (table 4.1) is the most common example of this. Finally there are some species (eg vanadium) which scatter almost totally incoherently, a useful property for normalisation of diffraction data (section 4.6.3).

4.6 Data Corrections

There are various factors in a ToF neutron diffraction experiment, arising from both the instrument and the sample, which alter the measured intensities and must be corrected for to obtain the DCS. These are described more fully in *The ATLAS Manual* (Soper et al 1989) and *The SANDALS Survival Guide* (Turner et al 1995).

The measured intensities for a sample in a container (I_{SC}) and for the empty container (I_C) are given respectively by the general equations:

$$\begin{aligned} I_{SC}(\lambda) &= \Phi(\lambda) E_d(\lambda) \Delta\Omega \left[N_s F_s(Q) A_{s,SC}(\lambda) + N_c F_c(Q) A_{c,SC}(\lambda) + MS_{SC}(\lambda) \right] \\ I_C(\lambda) &= \Phi(\lambda) E_d(\lambda) \Delta\Omega \left[N_c F_c(Q) A_{c,C}(\lambda) + MS_C(\lambda) \right] \end{aligned} \quad (4.23a,b)$$

where $\Phi(\lambda)$ is the neutron flux, $E_d(\lambda)$ the detector efficiency, $\Delta\Omega$ the solid angle occupied by the detector, N the number of atoms in the beam, $F(Q)$ the DCS which we wish to extract, $A(\lambda)$ the absorption correction and $MS(\lambda)$ the multiple scattering correction. The subscripts S,C and SC refer to the sample, the can and the sample plus can respectively.

This section outlines why these corrections occur and the mathematical approaches used to calculate them. The particular sequences of measurements and corrections which were used to extract the sample DCS from the measured data are described with the experiments in chapters 5 and 7.

4.6.1 Attenuation

Data must be corrected for absorption of neutrons by the sample. The intensity of a beam of radiation passing through an absorbing medium is reduced from its initial intensity by a factor of $e^{-\mu x}$, where x is the path length of the beam through the absorbing

medium and μ is the absorption coefficient, which for neutrons is wavelength dependant. The attenuation factor is calculated exactly for each wavelength, taking an average over the lengths of all possible paths through the sample.

4.6.2 Multiple Scattering

The multiple scattering from a sample cannot be calculated exactly as this would require the form of the single scattering (i.e. the DCS) to be known. It is calculated by assuming that the scattering at a particular wavelength is isotropic with respect to scattering angle and integrating over the sample volume (Soper et al 1989). This approximation is reasonable provided the sample scatters a small (<20%) fraction of the beam.

4.6.3 Normalisation to Vanadium

A distinctive advantage of neutron scattering is the possibility of normalisation to a standard sample, usually vanadium. The scattering from vanadium is almost completely incoherent with a few very weak Bragg peaks. These, along with the statistical noise, can be removed by fitting a curve through the data and ignoring regions with known Bragg peaks. After correction for multiple scattering and inelastic effects the smoothed incoherent scattering gives the shape in Q space of the combined instrumental corrections, including detector efficiency and area. These corrections are independent of the sample, and so we can remove them by dividing the sample data by the vanadium data. Knowing the number of scattering nuclei in both the vanadium and the sample also allows absolute normalisation of the data without the fitting procedures required in an X-ray diffraction experiment. Figure 4.6 shows a typical vanadium calibration spectrum.

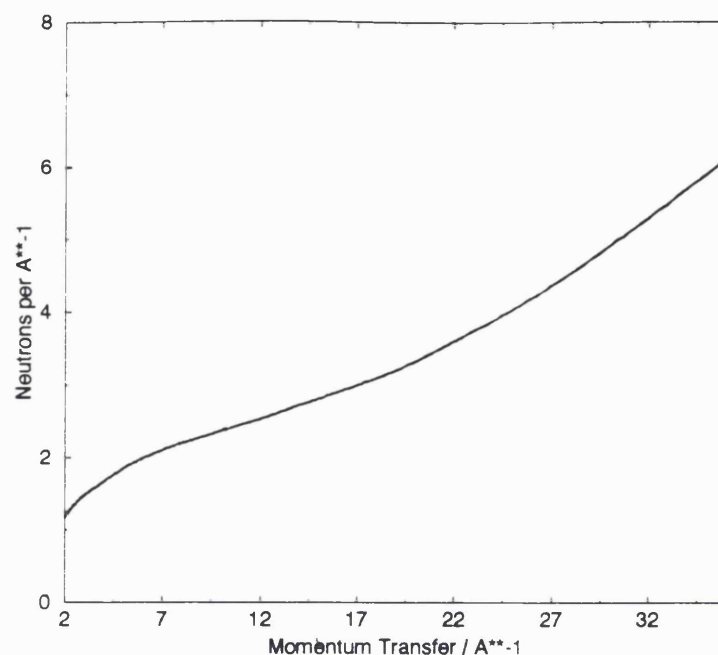


Figure 4.6. Vanadium calibration correction for the 35° detector bank on LAD. This was obtained from the scattering from a 3mm thick vanadium sheet at an angle of 75° to the neutron beam.

4.6.4 Inelastic (Placzek) Effects

In a diffraction experiment the energy of detected neutrons is not analysed and we assume that we are measuring $F(Q,0)$ (the Static Approximation, section 4.2.2). In practice inelastic scattering processes often occur due to recoil of nuclei under the impact of the neutrons, and a neutron can either lose or gain energy in its interaction with the sample. This is particularly significant in samples containing light atoms such as hydrogen or deuterium whose mass is comparable to that of the neutron and so have a greater recoil.

To calculate the inelastic correction requires knowledge of the form of the scattering but this can sometimes be approximated. The Placzek correction is a function of both Q and θ , is greatest at low Q and high θ , and affects the interference and self

scattering terms independently. The correction for the interference term cannot be calculated but is expected to be small (Soper et al 1989).

A Placzek correction was not found to be necessary for any of the data used in producing the results described in this thesis; several data sets collected at a high scattering angle ($\theta=75^\circ$) were however discarded because of the difficulty of calculating a Placzek correction (chapter 7).

4.6.5 Normalisation to The Incident Beam Flux

Correction for the wavelength dependency of the incident neutron flux is achieved using a low efficiency ($\sim 2\%$) detector placed in the incoming neutron beam to monitor both the total neutron count and the wavelength distribution. The data can then be normalised by dividing by the incident wavelength spectrum (figure 4.5).

4.6.6 Time-Independent Background

If there is a time-independent background then this leads to a non-linear background at low Q , which is inversely proportional to ToF. This kind of background can arise from electronic noise in the detectors, which is expected to be greater in scintillator detectors than in gas detectors, or from gamma rays being emitted from an activated sample such as vanadium. The time-independent background is calculated following the method outlined in *The Correction of ToF Neutron Scattering Spectra for Time-Independent Backgrounds* (Hannon 1996). This involves fitting to the shape of the neutron flux at long times of flight, given by:

$$y = Bt^{-4} + C \quad (4.24)$$

where y is the number of neutrons per unit time, t is the time of flight, B is a constant and C is the constant background.

4.6.7 Detector Deadtime

Data must be corrected for detector deadtime, the time after a detection event during which a detector and electronics are ‘busy’ recording that event and so unable to record another event. Although this time is small (typically $3\mu\text{s}$ for a ^3He detector or 250ns for a scintillator) detectors are wired together such that the detector electronics are dead after a detection event by any one of a group of detectors, so this can be a significant correction.

Interlayer Structure in Crystalline Alkyl-Ammonium Vermiculites

5.1 Contents

As described in chapter 3, the mechanism of macroscopic swelling of alkyl-ammonium vermiculites is poorly understood, and it is unclear why this phenomenon occurs when the counterion is PrNH_3 or BuNH_3 but not any other alkyl-ammonium ion. It has been suggested (Skipper et al 1995) that an essential precursor for macroscopic swelling is full hydration of the counterions, allowing them to leave the clay surface during the swelling process. A further question in the case of the alkyl-ammonium vermiculites is whether the counterions form bilayer or micelle like structures in the swollen phase, although this seems unlikely in view of the thermodynamic data presented in section 3.5. In order to distinguish between the possibilities it is necessary to measure the interlayer structures in the short chain ($n_c < 5$) alkyl-ammonium vermiculites, which have not previously been determined.

The interlayer structures in BuNH_3 and MeNH_3 Eucatex vermiculite were investigated to allow comparison between a swelling and a non-swelling vermiculite. The experiments were carried out using the LAD time of flight neutron diffractometer at the ISIS Pulsed Neutron Facility. This chapter describes these experiments, including: sample preparation; experimental details; data correction; data fitting procedure; results.

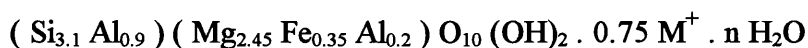
5.2 Sample Composition

The vermiculite used for the experiments is from Eucatex in Brazil and occurs naturally as macroscopic crystals, typically 5mm by 5mm in the plane of the clay layers and ~0.5mm thick. The unit cell of the clay is 5.28Å by 4.56Å in the plane of the clay layers. Because of the infinite possible variety of clay minerals there is still some uncertainty in both the layer composition and the layer charge. Samples of sodium Eucatex have been analysed and the composition found to be (Jinnai et al 1996)



where the species in the square brackets represent the clay layers, with 0.65 interlayer counterions per unit cell. This composition is consistent with overall electrical neutrality if all cations in the layer are assumed to be in their highest common oxidation state. The cation exchange capacity of sodium Eucatex has been measured by sodium adsorption spectroscopy (Humes 1985) and also found to be 0.65. Analyses of butyl-ammonium vermiculite by Unilever and the Kurare Co. (MV Smalley, unpublished results) have however have suggested counterion contents of 0.8 and 0.85.

There are two possible explanations for this inconsistency. Firstly, the presence of excess salt trapped in the clay crystals could lead to an overestimate of the layer charge (section 3.2.2). Secondly, reduction of Fe(III) to Fe(II) might occur in the clay layers, so increasing the layer charge. This hypothesis is supported by the observation that the butyl-ammonium gels sometimes change colour from brown to green, suggesting the formation of Fe(II). There is however no information as to the consistency of this effect between samples, or the extent to which it might occur in other alkyl-ammonium vermiculites. The composition of the samples was initially assumed (for data correction and fitting purposes) to be



with the sets of species in brackets representing the tetrahedral and octahedral cations respectively. The water content of MeNH₃ and BuNH₃ vermiculite was measured by weighing samples before and after drying in an oven at 80°C for 10hrs. The water content was found by this method to be 4.8 and 7.4 water molecules per unit cell respectively, although these figures probably include water trapped in faults in the clay samples in addition to the water absorbed between the clay sheets.

5.3 Sample Preparation and Container

Natural vermiculites contain a mixture of mono-valent and divalent counterions including K⁺ and Ca²⁺. In order to remove these the crystals were soaked for a year in a 1M NaCl(aq) solution at 60°C, the solution being changed every two weeks, to give sodium Eucatex. These crystals were subsequently exchanged for six months in a 1M (aq) solution of C₄H₉NH₃Cl to give n-butyl-ammonium Eucatex.

These crystals were then further exchanged for one month in solutions of three isotopic forms of each of the two counterions, methyl- and n-butyl-ammonium chloride: C₄H₉NH₃Cl / CH₃NH₃Cl ; C₄D₉NH₃Cl / CD₃NH₃Cl ; C₄H₉¹⁵NH₃Cl / CH₃¹⁵NH₃Cl. All of the solutions were prepared using standard reagents, with the exception of C₄H₉¹⁵NH₃Cl, which was too expensive to purchase. It was therefore synthesised by reaction of the acid chloride C₃H₇COCl with ¹⁵NH₄OH (aq) to give C₃H₇CO¹⁵NH₂, followed by reduction of this amide with LiAlH₄. The full procedure is given in Appendix A. This synthesis was successful, the product being verified using infrared absorption spectroscopy, but gave a very low yield. The C₄H₉¹⁵NH₃ vermiculite sample

therefore consisted of only a single 5mm x 5mm x 0.5mm crystal with an isotopic enrichment of ~60%.

Exchange of the samples was verified using X-ray diffraction to measure the layer spacing, which was found to be 12.3Å for MeNH₃ and 19.4Å for BuNH₃. The latter is consistent with the published layer spacing of 19.4Å for BuNH₃ Eucatex (Braganza et al 1990). Some of the isotopically unenriched crystals were then transferred from solutions containing H₂O to solutions containing D₂O. This gave a total of eight samples of Eucatex vermiculite containing the following species in the interlayer region:

- | | |
|---|---|
| 1. CH ₃ ^{nat} NH ₃ ⁺ / H ₂ O | 5. C ₄ H ₉ ^{nat} NH ₃ ⁺ / H ₂ O |
| 2. CD ₃ ^{nat} NH ₃ ⁺ / H ₂ O | 6. C ₄ D ₉ ^{nat} NH ₃ ⁺ / H ₂ O |
| 3. CH ₃ ¹⁵ NH ₃ ⁺ / H ₂ O | 7. C ₄ H ₉ ¹⁵ NH ₃ ⁺ / H ₂ O |
| 4. CH ₃ ^{nat} ND ₃ ⁺ / D ₂ O | 8. C ₄ H ₉ ^{nat} ND ₃ ⁺ / D ₂ O |

Unfortunately, due to the limited beam time available, the samples in D₂O had only 48 hours to exchange. Additionally samples 1, 6 and 7 were exchanged to D₂O before being transferred back into H₂O, and so may have contained a mixture of H₂O / D₂O. This made it difficult to assign absolute numbers of water molecules in the fitted interlayer structures (section 5.11).

Samples were loaded into the sample can as follows. The fully exchanged Eucatex crystals were removed from their soaking solution and sandwiched between two 0.3mm thick by 10cm square vanadium sheets, the clay layers being parallel to the sheets. Crystals were laid over an area covering at least 1cm by 1cm at the centre of the

sheets, an area which would be centred in the neutron beam. Typically 5-10 crystals were needed, depending on the individual dimensions of the crystals. The vanadium plates with the sample were mounted vertically inside a cylindrical aluminium sample can. This was ~30cm in diameter and had a thin window (~0.2mm thick) around the whole can at the level of the sample, so minimising absorption of the incident and diffracted neutron beams. A 50ml glass beaker containing H₂O or D₂O was placed in the bottom of the sample container to maintain the samples at 100% humidity, and the can vacuum sealed. The sample can and arrangement of the sample are shown in figure 5.1a and 5.1b.



Figure 5.1a. Picture of the sample container showing the vanadium plates and the cylindrical can in which they were sealed.

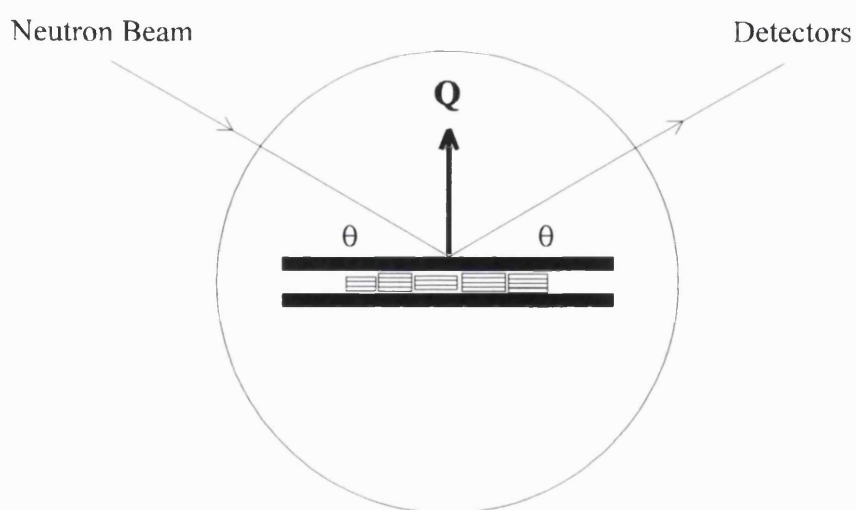


Figure 5.1b. Schematic view looking vertically down onto the sample can, showing the aluminium can with the 0.3mm vanadium plates and the clay crystals (not to scale). The orientation relative to the incoming (horizontal) neutron beam is shown.

5.4 The LAD Diffractometer and Data Collection

The experiments were carried out on the LAD diffractometer (figure 5.2) at the ISIS Pulsed Neutron Facility. LAD uses neutrons from a methane moderator at 100K, with wavelengths of 0.25 - 6.5Å. After collimation, an aperture was used to reduce the incident neutron beam to 10mm x 10mm, the beam being horizontally incident on the sample. There are seven pairs of detector banks positioned around the sample at angles of 5° to 150° in 2θ , which between them cover a continuous momentum transfer range of 0.08 - 50 Å⁻¹. The angle, resolution and Q range of each detector bank are listed in table 5.1. A particular detector bank will be specified by its angle (2θ).

Because the vermiculites are macroscopic single crystals the orientation of the sample with respect to the neutron beam and detector must be considered. The aim of these experiments was to investigate the structure perpendicular to the clay layers by measuring the scattering solely in this direction. To do this the sample must be orientated with the layers in a θ - θ geometry relative to the neutron beam and the detector bank, putting the momentum transfer vector perpendicular to the clay layers (figure 5.1b). At a given time only one detector bank can be positioned in this geometry. The Q range which can be investigated at any one time is therefore limited to that of the chosen detector bank, data from the other 13 banks being discarded. It would in theory be possible to investigate the structure parallel and perpendicular to the clay layers simultaneously, using a beam to sample angle of 45° and measuring in both the 90° detector banks. It was however decided to be more important to maximise the measured Q range in the limited time available than to measure the structure parallel to the clay layers.

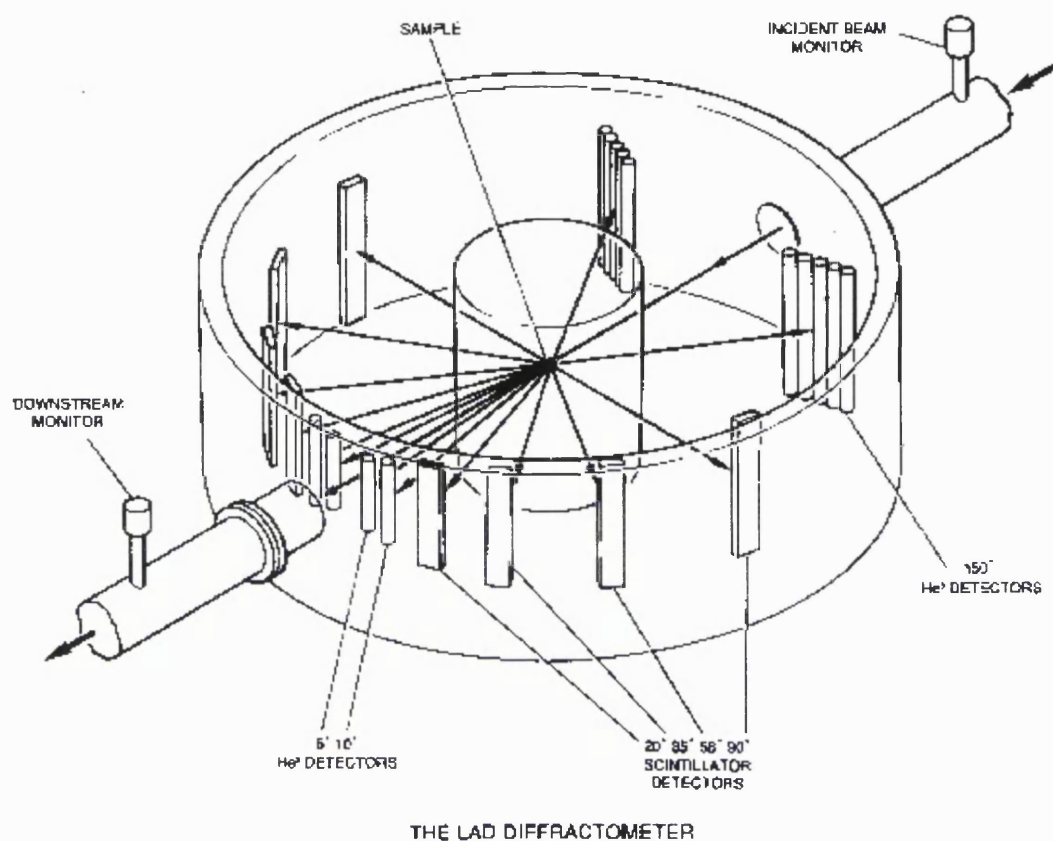


Figure 5.2. The LAD Diffractometer at the ISIS Facility (Source: ISIS web site)

Bank	Angle, $2\theta^\circ$	Resolution, $\Delta Q/Q$	Q range / $\text{\AA}^{-1}$	Detector type
1	± 5	14%	0.08 - 2.2	^3He
2	± 10	7%	0.17 - 4.4	^3He
3	± 20	3.5%	0.34 - 8.7	Scintillation
4	± 35	1.8%	0.58 - 15.1	Scintillation
5	± 58	1.2%	0.97 - 25.1	Scintillation
6	± 90	0.8%	1.36 - 35.5	Scintillation
7	± 148	0.6%	1.86 - 48.6	^3He

Table 5.1. Specifications of the LAD Diffractometer.

There are two reasons why data had to be collected over a wide Q range. On the one hand data must be collected at sufficiently low Q to cover the (001) Bragg reflection, but on the other hand the real space resolution of an experiment is limited by the high Q limit of the data ($Q_{\max}$), the resolution being given by (equation 4.11) $2\pi/Q_{\max}$.

Several data sets were collected for each sample, the can being orientated in the manner described using one detector bank after another. These were selected to maximise the total Q range while still giving a sufficient overlap in Q space between the data sets to allow them to be joined. For MeNH_3 vermiculite crystals the 150° and 20° banks were used; for BuNH_3 vermiculite crystals the 10° bank was also needed as the larger clay layer spacing means that the (001) reflection occurs at lower Q . Prior to each run the sample can was placed in approximately the required orientation and a rocking curve measured to maximise the measured intensity as follows. Data were collected for ~ 2 minutes and then the can was rotated in either direction in steps of $\sim 1^\circ$. The (001) Bragg peak intensities were then compared after normalisation to the total neutron count. The can was finally positioned to maximise the observed Bragg intensities. This position was in all cases found to be within $\pm 5^\circ$ of the nominal orientation, which is comparable with the expected mosaic spread of the crystals.

Data were collected for ~ 3 hours for the detector banks at 10° and 20° and ~ 8 hours for the 150° bank, better statistics being needed for the less intense higher order peaks seen in the data from the 150° bank. After these times all of the Bragg peaks could be clearly distinguished from the background noise. Typical data sets are shown in figure 5.3.

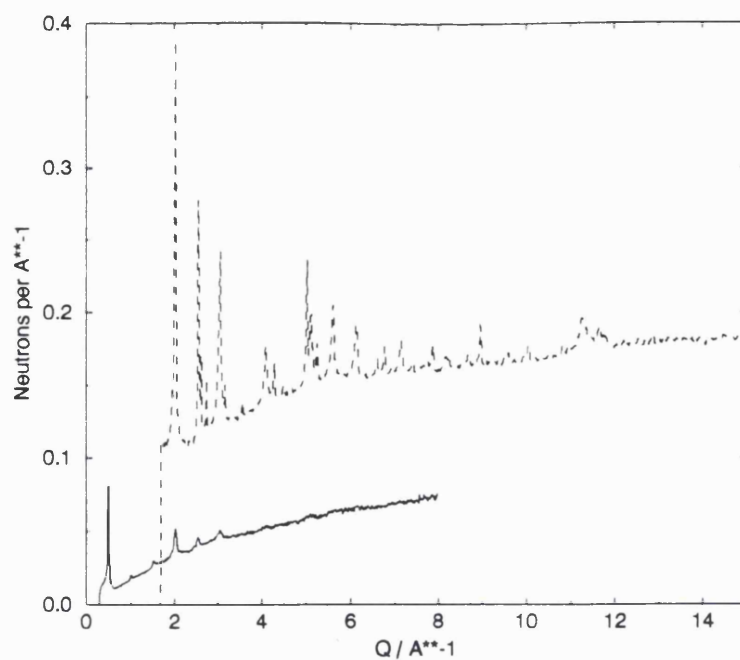


Figure 5.3. Data collected from the $\text{CH}_3\text{NH}_3 / \text{H}_2\text{O}$ sample at angles of 20° (solid line) and 150° (dashed line) in 2θ . The data have been converted from ToF to Q and divided by the incident wavelength spectrum (section 5.5).

5.5 Data Correction

To obtain $F(Q)$ for a sample four data sets were required, these being for: i) the sample in the can; ii) the empty aluminium sample can with vanadium plates (empty can run); iii) the aluminium can without the vanadium plates (background); iv) a 6mm vanadium rod. The sequence of corrections applied is shown in figure 5.4, the programs used to calculate each correction being shown in brackets. They are described more fully in *The ATLAS Manual* (Soper et al 1989). The operations performed by each of these programs are:

1) FLAT BACKGROUND. Time independent background corrections were calculated by fitting to the spectra at long ToF as described in section 4.6.6 (Hannon 1996).

2) NORM. The individual ToF spectra were corrected for detector dead time and the time independent background subtracted. The latter was found to have a significant effect only on the low Q part of the background and vanadium data sets. The spectra were then converted to wavelength and divided by the incident monitor spectrum. The data were finally converted to a momentum transfer scale.

3) CORAL. Absorption and multiple scattering corrections were calculated as a function of neutron wavelength for each of the samples, the empty container and the vanadium rod.

4) VANS. The vanadium calibration was calculated from the vanadium data as follows. The Bragg peaks and statistical noise were removed by fitting using Chebyshev polynomials. The data were then corrected for multiple scattering and Placzek effects.

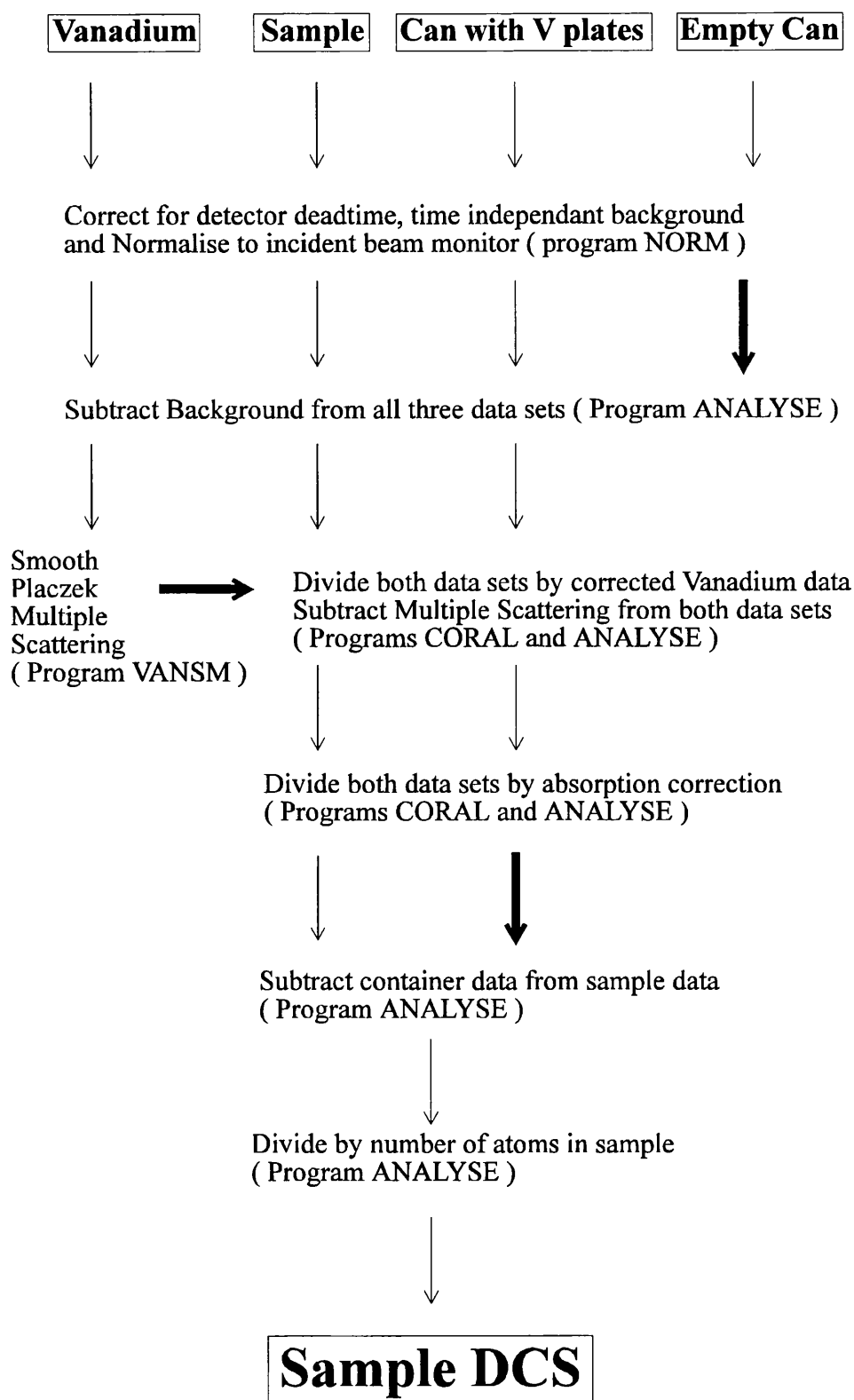


Figure 5.4. Sequence of corrections applied to obtain the sample differential cross section from the raw data. Boxed text refers to the data, unboxed text to operations applied to the data. Where arrows are shown in parallel this indicates that the operation below is applied to each data set in parallel; a bold arrow indicates that a data set is incorporated into the others in that operation.

5) ANALYSE. The results of programs NORM, CORAL and VANSIM were combined to calculate $F(Q)$ for each sample by the following sequence:

- i) Sample data: subtract the background, divide by the vanadium calibration and subtract the multiple scattering.
- ii) Empty can data: subtract the background, divide by the vanadium calibration, apply the can absorption correction and subtract the multiple scattering.
- iii) Subtract the can data from the sample data, apply the sample absorption correction and divide by the number of scattering nuclei in the sample.

5.6 Calculation of (00*l*) Bragg Peak Intensities

The (00*l*) Bragg intensities were obtained from the sample data sets by integrating above the background (incoherent) scattering level, this level being determined by inspection of each Bragg peak. The Bragg intensities are smaller in the data sets recorded at lower scattering angles because the mosaic spread of the sample covers a narrower range of Q space at higher scattering angles. This is illustrated in figure 5.5 which shows the corrected data sets for the $C_4H_9NH_3 / H_2O$ sample from the detector banks at 10° , 20° and 150° . The intensities of peaks in the 10° and 20° data sets were scaled to the intensities in the 150° data sets by multiplying by the ratio of areas of the most intense peak in the overlap region between data sets. For the $MeNH_3$ samples this was the (004) reflection; for the $BuNH_3$ samples the (006) was used to scale from 20° to 150° and either the (002) or (003) to scale from 10° to 20° . This procedure gave the relative intensities of the first 24 and 26 (00*l*) reflections for the $MeNH_3$ and $BuNH_3$ vermiculites respectively.

Figure 5.6 illustrates the differences created in the Bragg intensities by isotope substitution. This shows the (004) to (006) Bragg reflections for the $MeNH_3$ vermiculites in H_2O and D_2O (samples 5 and 8), clearly illustrating the suppression of the (005) peak relative to the (004) and (006) which is caused by deuteration.

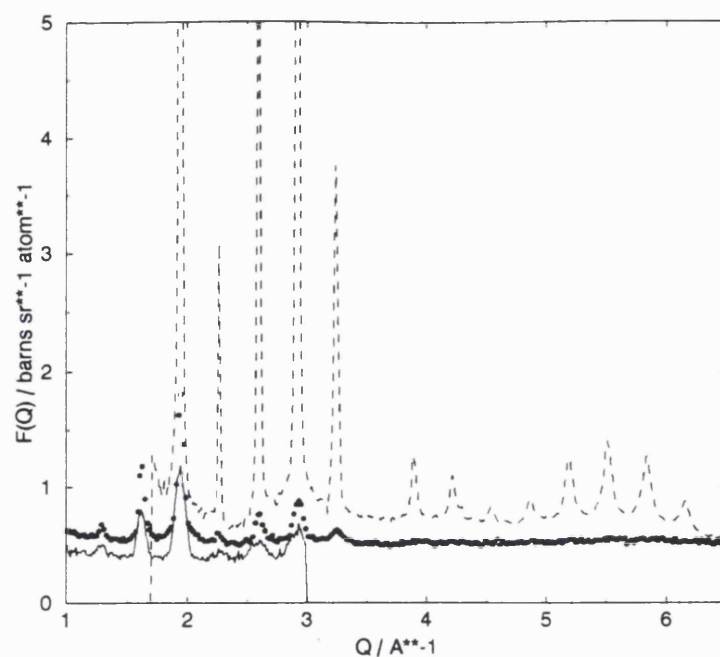


Figure 5.5. $F(Q)$ for $C_4H_9NH_3$ vermiculite measured at 10° (solid line), 20° (filled circles) and 150° (dashed line), showing i) the increase in absolute peak intensities at higher scattering angles, and ii) overlap of the data sets in Q space.

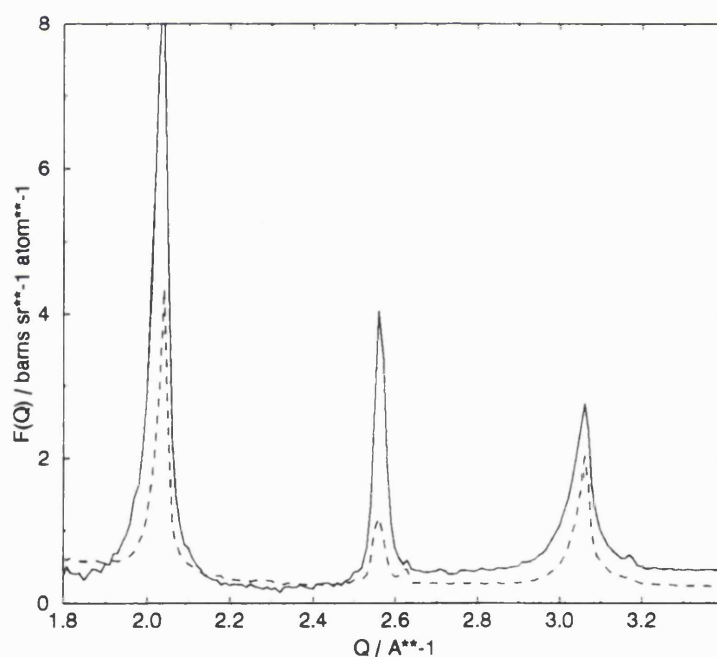


Figure 5.6. $F(Q)$ for CH_3NH_3 vermiculite in H_2O (solid line) and D_2O (dashed line), showing the (004) to (006) Bragg peaks.

5.7 Discussion of Errors and Uncertainties in The Data

The three main sources of error in the corrected data sets were:

- There is uncertainty in the precise angle between the sample can and the neutron beam.

This angle might not be the same as the angle between the sample and beam because of possible misalignment of the clay crystals between the vanadium sheets. This could be significant at 10° or 20° in 2θ .

- While calculating the corrections the samples were treated as solid rectangular blocks, while in practice they consist of a collection of irregular crystals whose size and shape differ from sample to sample.

- There is uncertainty in the composition of the samples.

- The neutron beam footprint is wider than the sample at small scattering angles.

These could lead to potentially large errors in the normalisation of the data, principally arising from the variation in the sample dimensions. For the purposes of the correction procedures the samples were treated as being 0.5mm thick and covering the 1cm by 1cm area of the beam, but this is an approximation as the samples consisted of irregular crystals packed together. The crystals were placed to give as even a covering of the beam as possible but there were inevitable variations in both the area covered by the sample and the thickness of different parts of the sample. In the case of the $\text{C}_4\text{H}_9^{15}\text{NH}_3$ sample this was compounded by the small number of clay crystals available. These errors however do not affect the relative intensities of the Bragg peaks within a data set or between data sets collected for the same sample at different angles. It was therefore assumed that the data sets were not properly normalised and a normalisation factor was included in the fitting routine (section 5.8). This was calculated independently for each data set, so minimising the effects of the errors discussed above.

Multiple scattering corrections were only applied to the data collected at 150° . They were calculated for data from detectors at 10° and 20° 2θ and found to be both small and constant to within 3% over the wavelength range of interest. They did not therefore significantly alter the relative intensities of the Bragg peaks.

An advantage of neutron diffraction is that the the data correction procedure can be tested by observing the shape of the incoherent scattering. This is expected to be independent of Q as it is simply a function of the sample composition (equation 4.8). This was observed to be the case (figure 5.7) but with two provisos.

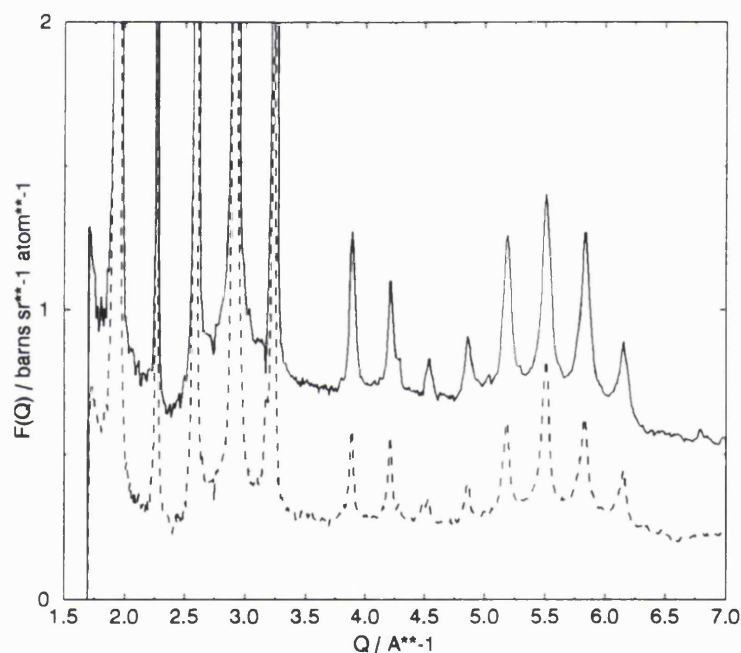


Figure 5.7. $F(Q)$ for $C_4H_9NH_3$ (solid line) and $C_4D_9NH_3$ (dashed line) vermiculite collected at an angle of 150° 2θ .

Firstly, a series of broad humps in the incoherent scattering were observed in all the 150° data sets around $3\text{\AA}$, $5.5\text{\AA}$ and $12\text{\AA}$. By dividing one data set by another it was established that there is a multiplying factor applied to the incoherent scattering which is Q dependent but independent of the sample. This indicates that the error has been

introduced by the vanadium normalisation, in which case this factor will affect the coherent intensities as well. Because the method used to fit a structure to the data relies on comparison of two data sets (section 5.8.1 below) systematic errors which affect all samples equally are less important than errors between samples, so this was within an acceptable level of error.

Secondly, an increase in the incoherent scattering level at $Q < 2\text{\AA}$ was observed in the 150° data (figure 5.7) but not in the 10° or 20° data (figure 5.5). This is due to inelastic scattering, which is expected to have a small effect on the coherent scattering (section 4.6.4). The Bragg peaks in this region were therefore simply integrated above the incoherent scattering level, this level being linearly interpolated between the levels on either side of the peak.

5.8 The Inverse Monte Carlo Fitting Procedure

As described in section 4.3.2 it is not possible to calculate the neutron scattering density profile between the clay layers directly from the Bragg intensities, since the sign of the structure factor cannot be observed in the data. In these experiments an Inverse Monte Carlo program written by Professor Alan Soper was used to fit density profile to the Bragg intensities. This program sets up a scattering density profile to simulate the clay and calculates Bragg intensities from this profile. A random change is then made to the profile, and if this change brings the calculated Bragg intensities closer to the observed intensities then the change is accepted. This process is repeated until the fit is optimised. Two of these scattering density profiles were fitted to the Bragg intensities for two isotopically different samples simultaneously, so allowing the position of the isotopically substituted species to be identified directly.

The density profile in a 1D crystal is related to the observed intensity by (section 4.3.2)

$$S(Q) = \int_0^d \rho(z) \cos(Qz) + i \rho(z) \sin(Qz) dz \quad (5.1a)$$

$$I(Q) = S^*(Q) S(Q) M(Q) \quad (5.1b)$$

where $\rho(z)$ is the scattering density at position z on the c^* axis and d is the layer spacing.

In the program two density profiles were set up using one dimensional arrays of movable particles, each of these particles having a Gaussian distribution of scattering density associated with it. The density profile in each array is then given by

$$\rho(z) = \sum_{i=1}^n e^{-\frac{(z-z_i)^2}{2f^2}} \quad (5.2)$$

where z_i is the position of the i^{th} particle and $f = 0.12\text{\AA}$, corresponding to the real space resolution of the experiment ($Q_{\text{max}} = 50\text{\AA}^{-1}$). Two profiles were set up, $\rho(z)_1$ and $\rho(z)_2$. The length of both was equal to the layer spacing of the sample, calculated from the position of the (001) Bragg peak. The layer spacing was found to be $12.3\text{\AA}$ for the methyl- and $19.4\text{\AA}$ for butyl-ammonium samples, which is consistent with the results from X-ray diffraction. The two profiles were combined (equation 5.3) to produce density profiles for two samples, $\rho(z)_a$ and $\rho(z)_b$

$$\rho(z)_a = \rho(z)_1 + b_a \rho(z)_2 \quad (5.3a)$$

$$\rho(z)_b = \rho(z)_1 + b_b \rho(z)_2 \quad (5.3b)$$

where b_a and b_b are the scattering lengths of the two isotopes of the species substituted between the two samples. The density profile $\rho(z)_1$ then represents the contribution to the total scattering density profiles from atoms in common between two samples, while $\rho(z)_2$ represents the contribution from the substituted atoms. These will be called the common profile and the difference profile respectively.

The density profiles $\rho(z)_a$ and $\rho(z)_b$, representing the two samples, were used to calculate (00*l*) Bragg intensities using equations 5.1a and 5.1b. The particles were then moved randomly to fit the calculated intensities to the measured intensities for both samples simultaneously. This was done by defining a variable χ^2 (the R-factor) by

$$\chi^2 = \sum_{1,l} \left(I(Q)_{\text{meas}} - N I(Q)_{\text{calc}} \right)^2 \quad (5.4)$$

where $I(Q)_{\text{calc}}$ is calculated from equations 5.1a and 5.1b, N is a normalisation constant calculated separately for each data set to optimise the fit and the summation is taken over the (001) to (00*l*) Bragg reflections where l is the highest order measured. A standard Monte Carlo procedure was used to decide whether to accept or reject

individual moves. If a move reduces χ^2 then it is accepted. If a move increases χ^2 then it is given an acceptance probability (p) based on the increase in χ^2

$$p = \exp \left(\frac{\Delta(\chi^2)}{(0.9\overline{\chi})^2} \right) \quad (5.5)$$

The fitting program was run until the R-factors (χ^2_1 and χ^2_2) and the normalisation constants (N_1 and N_2) for both data sets were observed to converge, this taking typically 10^5 to 10^6 moves. The final value of the R-factors are expressed as percentages, calculated by dividing the R-factor by the square of the Bragg intensities (averaged over the 001 to 00 l peaks) and multiplying by 100.

5.8.1 Errors and Uncertainties in The Fitting Procedure

While specific errors in the results are discussed in section 5.11 there are a number of general considerations which arise from this fitting procedure. It has already been outlined in section 5.7 how it is only necessary to obtain relative rather than absolute Bragg intensities, by the inclusion of a scaling constant in the comparison of the measured and calculated intensities. A further advantage is that the difference profile is fitted to differences in two data sets, so systematic errors in the experiment are cancelled out in the fit.

The effect of errors in the data was investigated by altering individual intensities to simulate the degree of errors discussed in section 5.6. It was found that this affected the areas of peaks in the fitted density profiles, but that the position of these peaks was robust. There are also two good tests of the reliability of the final fit. Firstly, the positions and scattering lengths of atoms in the clay layers are well known, providing a very useful test of any fitted density profiles. Secondly a fit can be tested by varying the

parameters in the routine to ensure that features in the fits are robust. These are detailed below.

5.8.2 The Form Factor

The form factor $M(Q)$ in equation 5.1b is a Lorentzian which the calculated values of $I(Q)$ were multiplied by to allow for the decrease in peak intensity at high Q due to the mosaic spread of the sample (section 4.3.4). $M(Q)$ was given by

$$M(Q) = \frac{1}{1 + \frac{Q^2}{\sigma^2}} \quad (5.6)$$

with σ being treated as a fitting parameter. All the fits were tested by varying σ and it was found that this affected the R-factors and the normalisation constants, the fit typically being optimised when $\sigma = 0.35$. It was found however that variations in σ had a negligible effect on the actual density profiles, even in the case of large variations in σ , as the changes produced in the relative calculated Bragg intensities are small.

5.8.3 Total Scattering Length Density and The Flat Background

If the fitting arrays contain more scattering density than is present in the real unit cell then there are two possible ways in which the fitting procedure might respond. Firstly, because the structure factor is a measure of the size of oscillations in the scattering density profile, not of the absolute scattering density, the excess could be left as a flat background which does not contribute to the structure factor. Secondly the excess could be used to scale up the whole of the fitted density profile. This would have an identical multiplicative effect on all of the calculated intensities. This effect would be

incorporated into the normalisation constant and so would not affect the quality of the fit.

Because of uncertainty in the sample composition it was necessary to have an excess of intensity present in the arrays. To avoid exaggeration of features in the manner described above, the particles were initially distributed evenly across both arrays, with the exception of peaks of suitable intensities placed to represent a unit cell of the clay layer. Any peaks developed by the fitting routine were therefore automatically normalised to these, the excess density being left as a flat background. The 'clay layer' peaks were not however fixed at their initial positions, as this would have prevented validation of the fits from the correct fitting of the clay layer. They were however constrained within $\pm 0.2\text{\AA}$ of their initial positions to prevent the fit from deviating too far from the known clay layer structure.

A second reason for having a non-zero background is that negatively scattering hydrogen nuclei can be fitted as dips below this background level. If the non-zero background were not present it would be necessary to have both positive and negative density in the fitting arrays in order to reproduce the actual density profiles in the samples.

For all fits the effect of altering the total scattering density in the fitting arrays was investigated to ensure that peaks in the fits were independent of the background level. By adding a large excess of intensity it was also possible to ensure that no features were being omitted from the fitted profiles because of an inadequate amount of scattering density in the arrays.

5.9 The Fits to the Data

Density profiles were fitted for 6 pairs of samples, as listed in table 5.2. These fits allowed three components to be located in each system:

- The alkyl protons
- The water and ammonium protons (the later exchange rapidly in water)
- The ammonium nitrogen atoms

Table 5.3 lists the parameters for each of these fits. The R-factors for all of the fits were less than 2.5%. A full fit to two sets of (00/) Bragg intensities is shown in figure 5.8.

Fit	Sample 1	Sample 2	Species in Substituted profile
1	$\text{CD}_3^{\text{nat}}\text{NH}_3^+$ in H_2O	$\text{CH}_3^{\text{nat}}\text{NH}_3^+$ in H_2O	Alkyl protons on methyl group
2	$\text{CH}_3^{\text{nat}}\text{ND}_3^+$ in D_2O	$\text{CH}_3^{\text{nat}}\text{NH}_3^+$ in H_2O	Water and ammonium protons
3	$\text{CH}_3^{15}\text{NH}_3^+$ in H_2O	$\text{CH}_3^{\text{nat}}\text{NH}_3^+$ in H_2O	Ammonium nitrogen
4	$\text{C}_4\text{D}_9^{\text{nat}}\text{NH}_3^+$ in H_2O	$\text{C}_4\text{H}_9^{\text{nat}}\text{NH}_3^+$ in H_2O	Alkyl protons on butyl group
5	$\text{C}_4\text{H}_9^{\text{nat}}\text{ND}_3^+$ in D_2O	$\text{C}_4\text{H}_9^{\text{nat}}\text{NH}_3^+$ in H_2O	Water and ammonium protons
6	$\text{C}_4\text{H}_9^{15}\text{NH}_3^+$ in H_2O	$\text{C}_4\text{H}_9^{\text{nat}}\text{NH}_3^+$ in H_2O	Ammonium nitrogen

Table 5.2. List of the sample pairs for which differences were fitted, with the species that are located by the difference profile in each case.

Parameter	Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6
I_a	18.13	18.13	18.13	18.07	18.07	18.07
bg_a	0.47	0.46	0.87	0.3	0.08	0.35
I_b	1.14	3.25	5.00	4.5	10.00	0.50
bg_b	0.05	0.073	0.40	0.09	0.33	0.026
σ	0.20	0.25	0.30	0.35	0.35	0.40
χ^2_1	2.16	2.36	2.12	1.77	1.01	1.24
χ^2_2	1.73	1.46	1.88	1.53	0.89	1.04
N_1	1.64	0.39	0.55	0.45	0.59	0.68
N_2	1.79	1.03	0.50	1.74	1.66	1.48

Table 5.3. Fitting parameters for each pair of data sets. $I_{a/b}$ is the total intensity put into the first and second arrays; $bg_{a/b}$ the flat background level in the common and difference fits; σ the fitting parameter for the form factor $M(Q)$; $\chi^2_{1/2}$ the R-factor for each data set and $N_{1/2}$ the fitted normalisation constant for each data set.

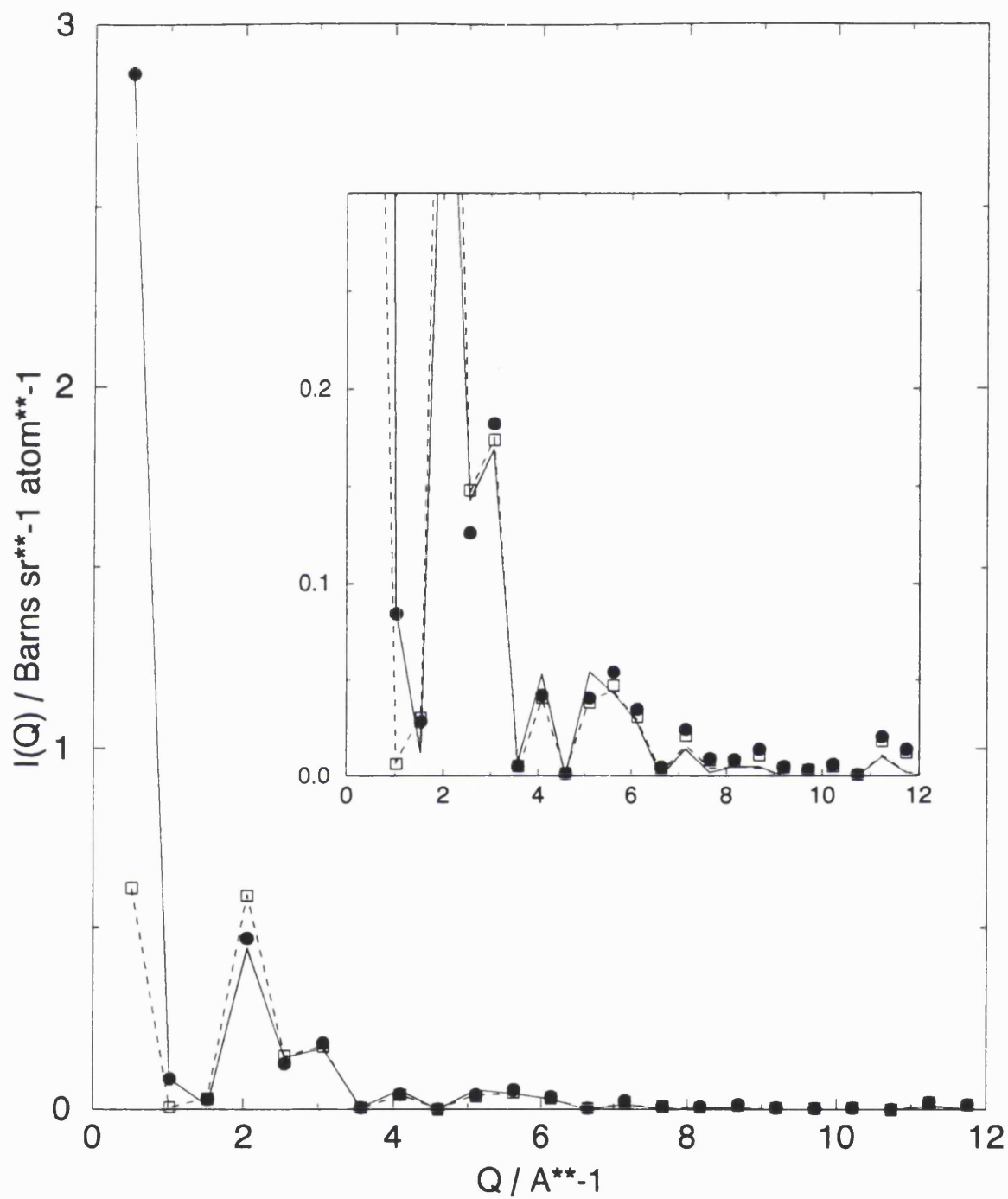


Figure 5.8. Comparison of the measured and calculated Bragg intensities as a function of Q for fit 1. The fit is shown for both samples: $\text{CH}_3^{\text{nat}}\text{NH}_3^+ / \text{H}_2\text{O}$ (measured - solid line, calculated - filled circles) and $\text{CD}_3^{\text{nat}}\text{NH}_3^+$ in H_2O (measured - dotted line, calculated - squares).

5.10 Results

The common and difference profiles for each of the six fits are plotted, with the flat backgrounds subtracted, in figures 5.9 - 5.14. The origin on the z axis has been set at the plane of the octahedral cations. This is the standard format in the literature and assists in visualising the interlayer structures, although it is arbitrary as regards the fitting procedure. The profiles have been smoothed by averaging over the final 10^4 steps in the fitting procedure.

The background levels in the common profiles were determined by integrating over the regions of the unit cell containing the clay layer and then setting the background level to give the correct peak areas for the known clay layer composition. Ideally this procedure would have been carried out using only the peaks due to oxygen atoms in the clay layers, as there is some uncertainty as to the composition of both the tetrahedral and the octahedral cations. However, because none of the clay oxygen peaks were completely resolved from the clay cation peaks, the integration was carried out between $0.0\text{\AA}$ and $1.75\text{\AA}$, a region representing half of the octahedral sheet. The background levels in the difference profiles were determined by visual inspection on the basis that there should be no real features in the difference profile in the $0.0\text{-}1.75\text{\AA}$ region.

Peaks in the profiles were then integrated relative to these background levels to give the sum of the scattering lengths of species in each part of the system. These are shown in tables 5.4-5.9, these being shown with the appropriate density profiles. Each table is divided into two parts. Peaks listed in the upper part are those which occur in the clay layer region and so are due to the clay layer plus any water absorbed into the hexagonal cavities on the clay surface. This region is taken as extending from 0 to $4.8\text{\AA}$, the position of the van der Waals surface of the surface (basal) oxygen atoms of the clay

layer. Peaks in the lower part are those in the interlayer region which are due to water and counterions. Because the unit cell is symmetrical along the z axis every peak has an equivalent peak at the opposite side of the unit cell. Only peaks positioned between $z = 0$ and $z = d/2\text{\AA}$ are listed. The exception to this are peaks which lie cross the centre of the unit cell, which have been integrated over their full width.

The final column of each table shows the assignment of numbers of atoms (and therefore of ions or water molecules) to each peak. Where a number in brackets is shown it represents the residual sum of scattering lengths after the species listed are accounted for.

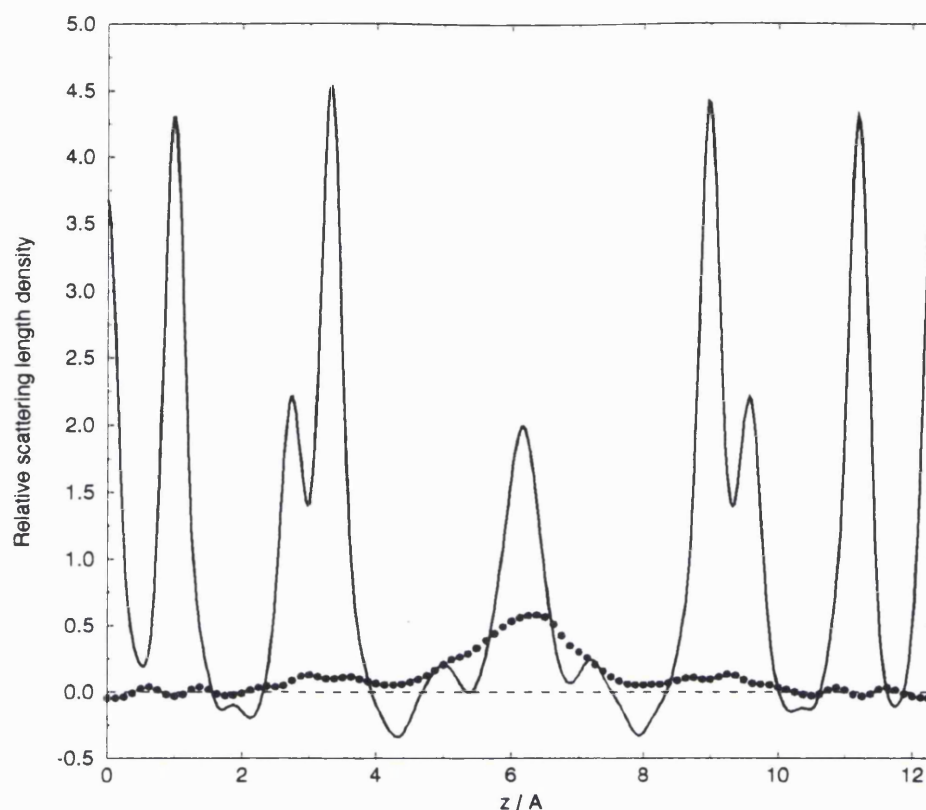


Figure 5.9. Fitted common (line) and difference (filled circles) components of the scattering length density profile in CH_3NH_3 and CD_3NH_3 vermiculite in H_2O (fit 1) as a function of position on the clay c^* axis. The origin is set at the centre of a clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 1.75	O_h Cations, O (Clay)	Common	2.61	O_h cations, 3 O
1.75 - 2.35	H (clay)	Common	-0.04	0.1 H
2.35 - 4.0	T_h cations, O (clay), H_2O	Common	2.89	T_h cations, 3 O, (0.36)
4.0 - 4.8	H (H_2O)	Common	-0.09	0.3 H
4.8 - 7.5	H_2O , C- NH_3	Common	1.62	0.65 C- NH_3^+ , (1.24)
4.2 - 7.9	H / D (alkyl)	Difference	1.06	0.6 H_3

Table 5.4. Analysis of peak areas in the fitted neutron scattering density profiles in figure 5.9 showing the limits of integration ($\text{\AA}$); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area (10^{-14}m); the number of atoms corresponding to these areas.

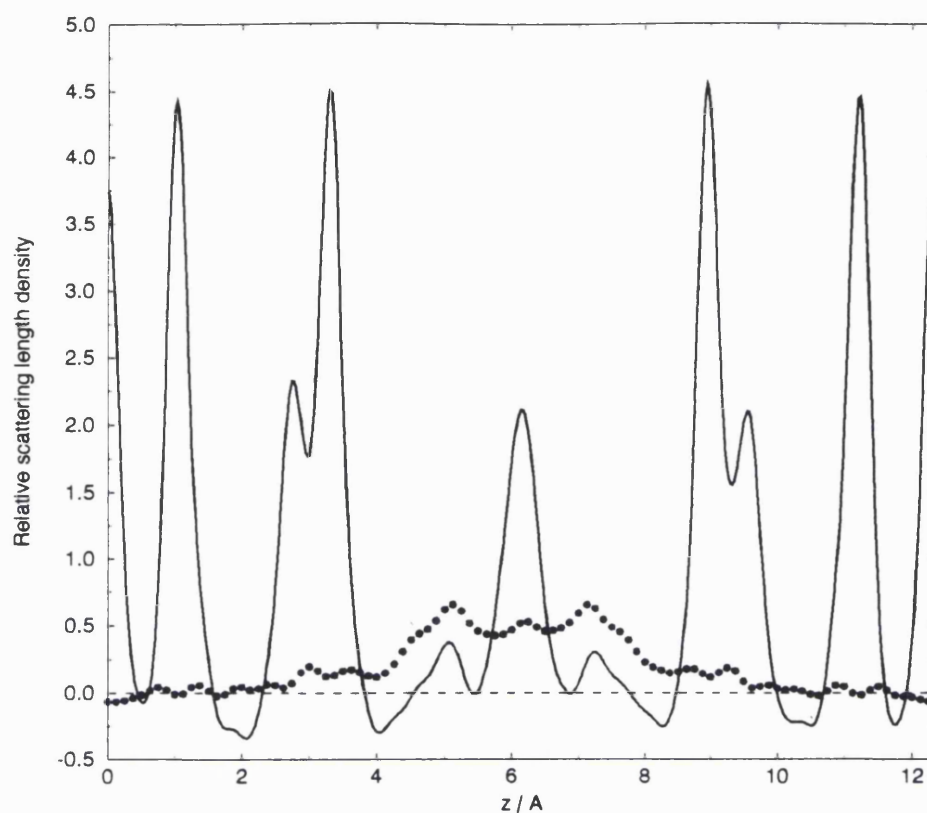


Figure 5.10. Fitted common (line) and difference (filled circles) components of the scattering length density profile in CH_3NH_3 vermiculite in H_2O and D_2O (fit 2) as a function of position on the clay c^* axis. The origin is set at the centre of a clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 1.75	O_h Cations, O (clay)	Common	2.61	O_h cations, 3 O
1.75 - 2.35	H (clay)	Common	-0.11	0.3 H
2.35 - 3.8	T_h cations, O (clay, H_2O)	Common	2.93	T_h cations, 3 O, (0.40)
3.8 - 4.8	H (H_2O)	Common	-0.04	0.1 H
1.5 - 4.8	H / D (H_2O)	Difference	0.47	0.8 H
4.8 - 7.5	O (H_2O), CH_3N	Common	1.66	0.65 CH_3N^+ , (1.28)
4.8 - 7.5	H / D (H_2O , NH_3)	Difference	1.42	2.5 H

Table 5.5. Analysis of peak areas in the fitted neutron scattering density profiles in figure 5.10 showing the limits of integration ($\text{\AA}$); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area (10^{-14}m); the number of atoms corresponding to these areas.

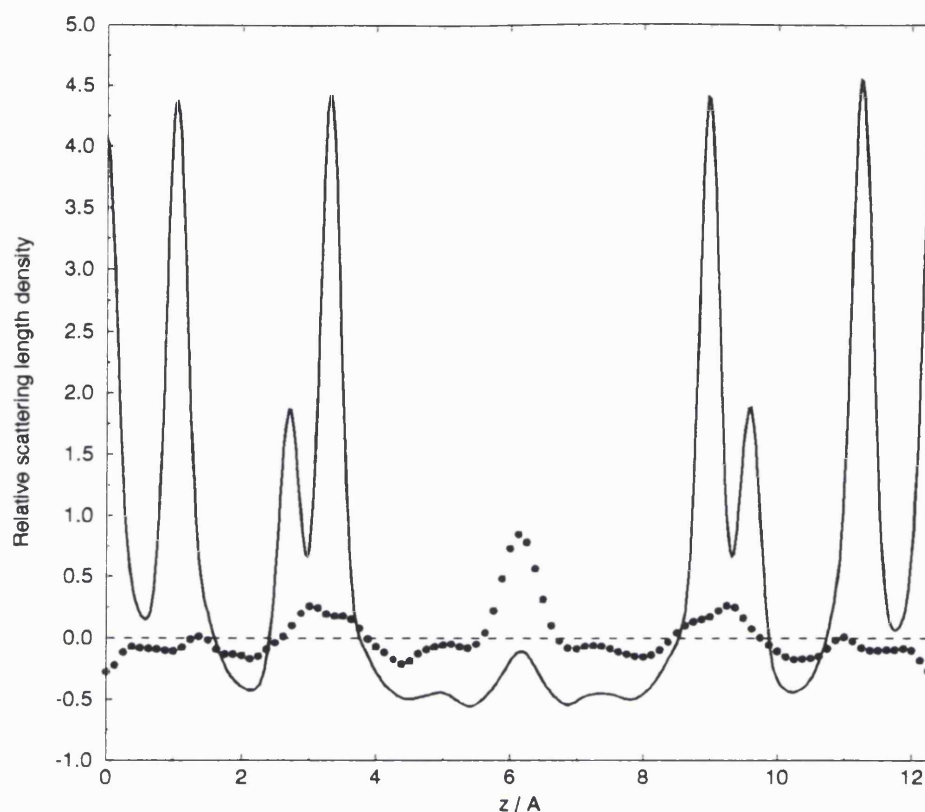


Figure 5.11. Fitted common (line) and difference (filled circles) components of the scattering length density profile in $\text{CH}_3^{\text{nat}}\text{NH}_3$ and $\text{CH}_3^{15}\text{NH}_3$ vermiculite in H_2O (fit 3) as a function of position on the clay c^* axis. The origin is set at the centre of a clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 1.75	O_h Cations, O (Clay)	Common	2.63	O_h cations, 3 O
1.75 - 2.35	H (clay)	Common	-0.21	0.6 H
2.35 - 3.8	T_h cations, O (clay), H_2O	Common	2.24	T_h cations, 3 O, (-0.29)
3.8 - 4.8	H (H_2O)	Common	-0.39	1.2 H
4.8 - 7.5	H_2O , CH_3NH_3	Common	-1.20	0.65 $\text{CH}_3\text{-H}_3^+$, (-0.32)
4.8 - 7.5	N (NH_3)	Difference	0.39	0.65 N

Table 5.6. Analysis of peak areas in the fitted neutron scattering density profiles in figure 5.11 showing the limits of integration ($\text{\AA}$); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area (10^{-14}m); the number of atoms corresponding to these areas.

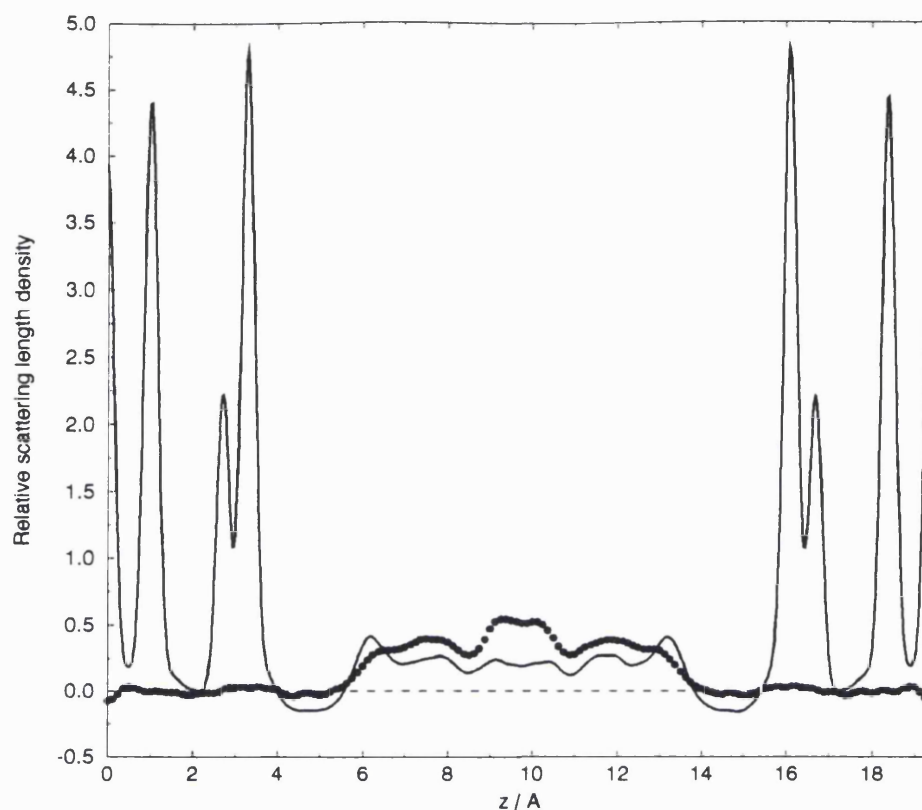


Figure 5.12. Fitted common (line) and difference (filled circles) components of the scattering length density profile in $\text{C}_4\text{H}_9\text{NH}_3$ and $\text{C}_4\text{D}_9\text{NH}_3$ vermiculite (fit 4) as a function of position on the clay c^* axis. The origin is set at the centre of a clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 1.75	O_h Cations, O (Clay)	Common	2.62	O_h cations, 3 O
1.75 - 4.0	T_h cations, O (clay), H_2O	Common	2.73	T_h cations, 3 O, (0.20)
4.0 - 5.5	H (H_2O)	Common	-0.18	0.5 H
5.5 - 13.9	H_2O , $\text{C}_4\text{-NH}_3$	Common	1.87	$0.75 \text{ C}_4\text{-NH}_3^+$, (-0.07)
4.8 - 14.6	H / D (alkyl)	Difference	2.78	0.5 H_9

Table 5.7. Analysis of peak areas in the fitted neutron scattering density profiles in figure 5.12 showing the limits of integration ($\text{\AA}$); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area (10^{-14}m); the number of atoms corresponding to these areas.

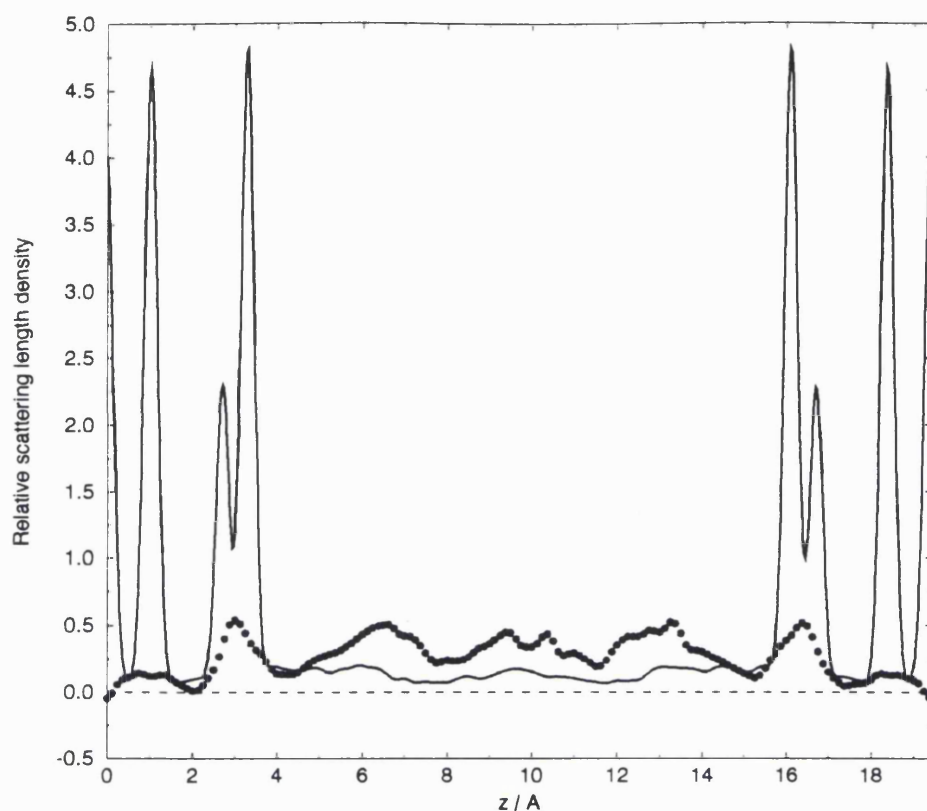


Figure 5.13. Fitted common (line) and difference (filled circles) components of the scattering length density profile in $\text{C}_4\text{H}_9\text{NH}_3$ vermiculite in H_2O and D_2O (fit 5) as a function of position on the clay c^* axis. The origin is set at the centre of a clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 1.75	O_h Cations, Clay Oxygen	Common	2.62	O_h cations, 3 O
1.75 - 4.8	T_h cations, O (clay, H_2O)	Common	3.00	T_h cations, 3 O, (0.47)
0.0 - 4.8	H / D (H_2O , NH_3)	Difference	0.68	1.2 H
4.8 - 14.6	O (H_2O), $\text{C}_4\text{H}_9\text{N}$	Common	1.29	0.75 $\text{C}_4\text{H}_9\text{N}$, (0.87)
4.8 - 14.6	H / D (H_2O , NH_3)	Difference	3.42	5.9 H

Table 5.8. Analysis of peak areas in the fitted neutron scattering density profiles in figure 5.13 showing the limits of integration ($\text{\AA}$); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area (10^{-14}m); the number of atoms corresponding to these areas.

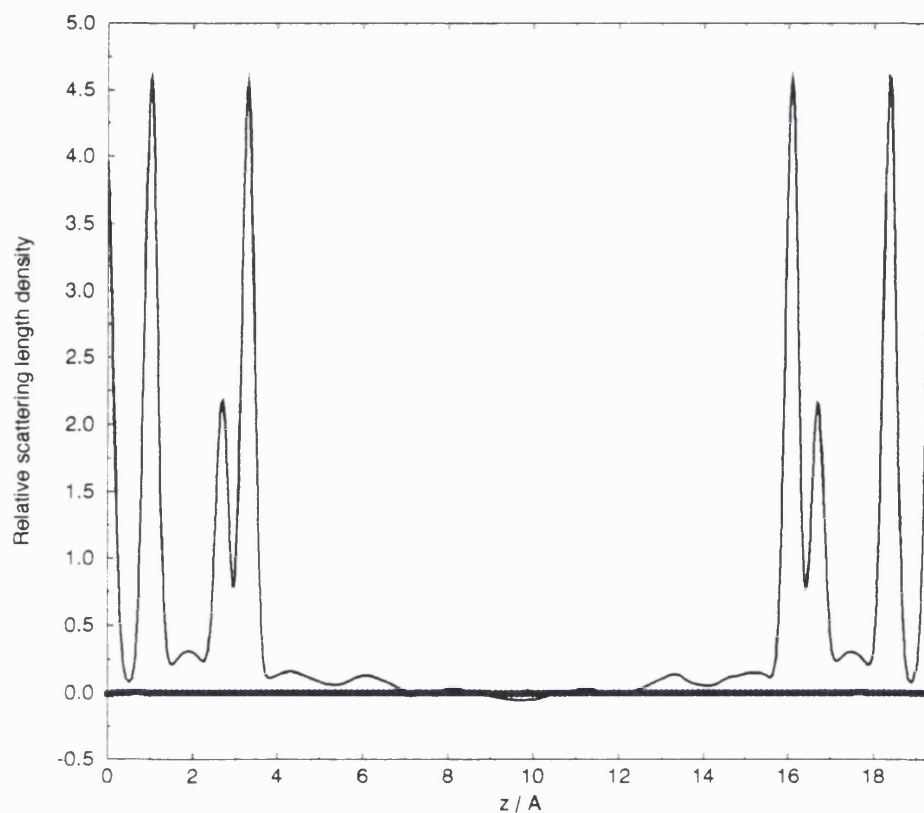


Figure 5.14. Fitted common (line) and difference (filled circles) components of the scattering length density profile in $\text{C}_4\text{H}_9^{\text{nat}}\text{NH}_3$ and $\text{C}_4\text{H}_9^{15}\text{NH}_3$ vermiculite (fit 6) as a function of position on the clay c^* axis. The origin is set at the centre of a clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 1.75	O_h Cations, O (Clay)	Common	2.62	O_h cations, 3 O
1.75 - 4.8	T_h cations, O (clay), H_2O	Common	2.84	T_h cations, 3 O, (0.31)
4.8 - 14.6	$\text{C}_4\text{H}_9\text{NH}_3$, H_2O	Common	0.35	$0.75 \text{ C}_4\text{H}_9\text{NH}_3^+$, (0.66)
4.8 - 14.6	Not fitted	Difference	0.0	-

Table 5.9. Analysis of peak areas in the fitted neutron scattering density profiles in figure 5.12 showing the limits of integration ($\text{\AA}$); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area (10^{-14}m); the number of atoms corresponding to these areas.

5.11 Errors and Uncertainties in The Density Profiles

The fitted density profiles are plotted with error bars in figures 5.15a to 5.15f. The errors are generally small compared to the size of features in the profiles, although it can be seen that they are large for certain features in the interlayer region (figure 5.15b for example). However, the density profiles are interpreted (section 5.12) principally from the qualitative consistency of features in the profiles, with less reliance on peak areas. There are two main reasons why the presence of any errors make a quantitative assignment difficult:

I) Uncertainty of the composition of almost all parts of the system, as described in section 5.2, makes it difficult to assign specific numbers of water molecules or counterions to peaks in the profiles. The most important factor is the assumption that 100% deuteration had taken place in the samples prepared in D_2O , as the negative scattering from any residual hydrogen would cause a large difference in the total scattering profile. Deuteration could be incomplete, but furthermore there could be a variable amount of deuterium present in different parts of the system: exchange of the clay hydroxyl groups or of water absorbed into the clay cavities might well be slower than in water hydrating the ions. This is almost certainly the case for the hydroxyl protons, which are known in sodium smectites to require extreme conditions for exchange (Hawkins and Egelstaff 1980). The fitted density profiles contain no indication of exchange having taken place on the hydroxyl groups (figures 5.10 and 5.13). It is also possible that fractionation of deuterium between different sites might occur (Suzuoki and Epstein 1976). Finally it is possible that some D_2O might have been present in samples 1, 6 and 7 after the transfer of these samples to D_2O and then back to H_2O (section 5.2).

II) Because hydrogen has a negative neutron scattering length, while carbon, oxygen and nitrogen have positive scattering lengths, the total scattering from most of the unsubstituted interlayer groups is very small (H_2O , $-0.08 \times 10^{-14}\text{m}$; CH_2 , $0.008 \times 10^{-14}\text{m}$; and NH_3 , $0.08 \times 10^{-14}\text{m}$). This is a disadvantage in accurately assigning numbers of species to peaks in the unsubstituted profiles, particularly in the case of water. It is however an advantage in that we expect any features in an H / D difference profile to be accompanied by corresponding features developed in the common profile, resulting from C/N/O atoms in the same group. This is a good check on whether features in the fits are reliable.

Comparison of the three fits for each system allows a test of the level of errors. The total scattering density profile for the unsubstituted sample can be calculated from each pair of profiles using equation 5.3. This gives three different profiles which in the complete absence of errors would be identical. The consistency of these was taken as an indication of the reliability of the fits (figure 5.16). Both sets show good qualitative consistency: the only feature that appears to be spurious is the peak/dip around 5.4 and $14\text{\AA}$ in the $\text{BuNH}_3 \text{H}_9/\text{D}_9$ unsubstituted profile (figure 5.12) which is not reproduced in the other profiles (figure 5.16b). The quantitative consistency between the fits shows some errors, especially for the $^{15}\text{N}/^{nat}\text{N}$ fits. In the context of points 1) and 2) above these errors prevent a detailed quantitative assignment of species to peak areas.

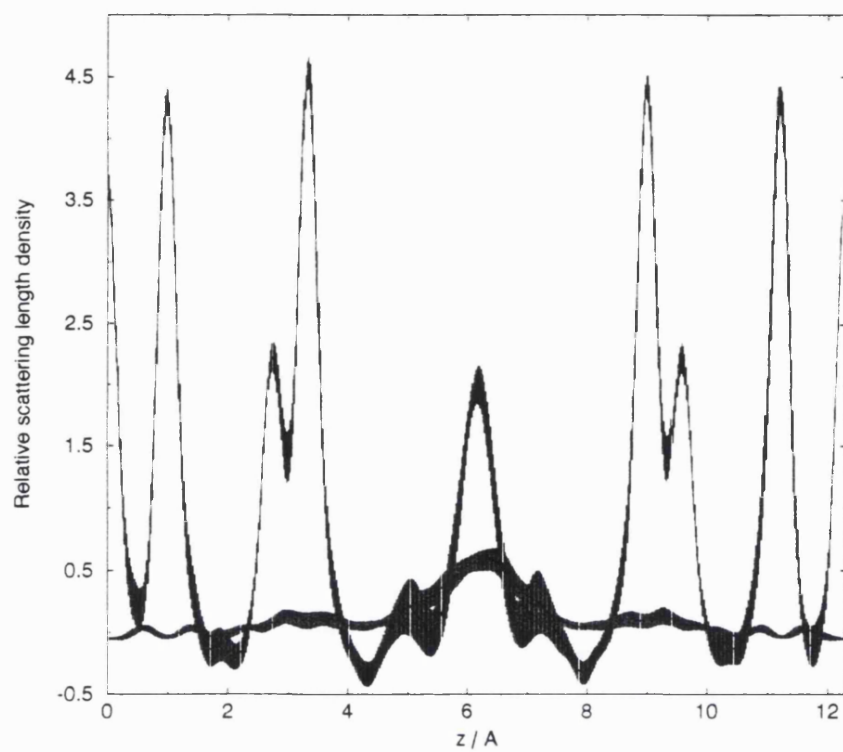


Figure 5.15a. Fitted density profiles for CH_3NH_3 and CD_3NH_3 vermiculite (fit 1)

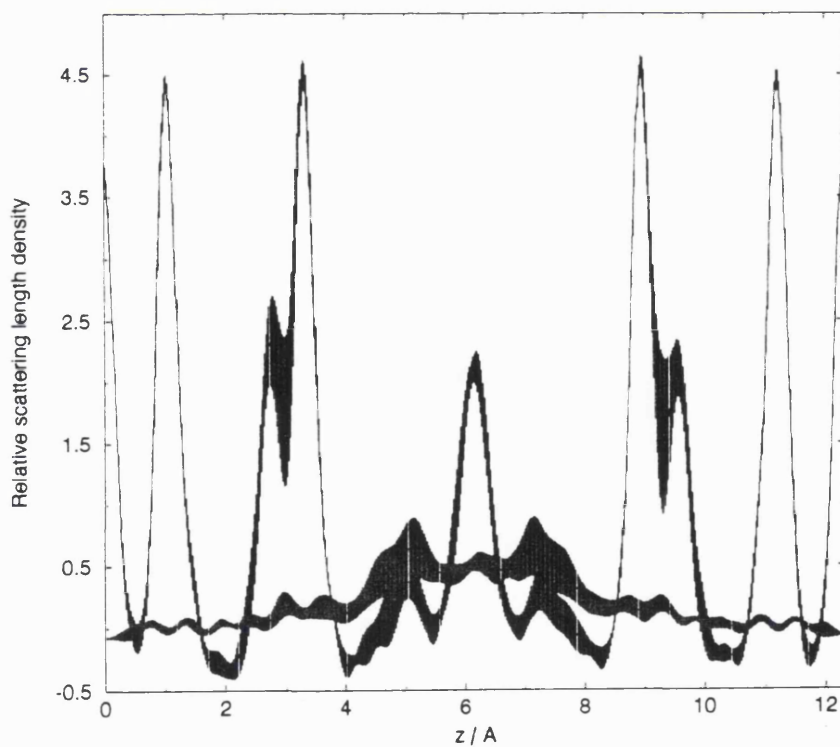


Figure 5.15b. Fitted density profiles for CH_3NH_3 and CH_3ND_3 vermiculite (fit 2)

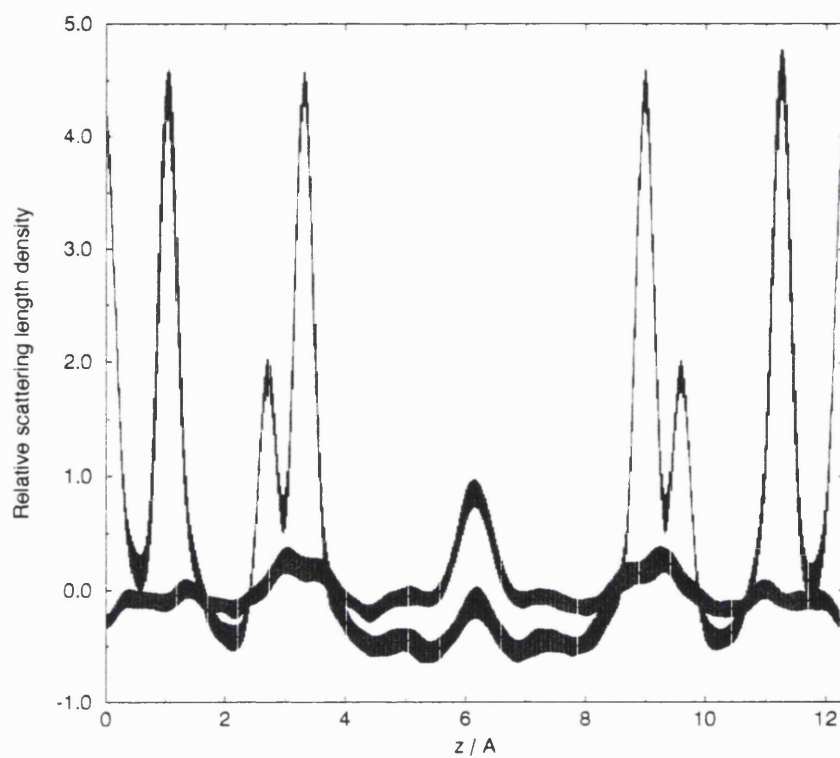


Figure 5.15c. Fitted density profiles for CH_3NH_3 and $\text{CH}_3^{15}\text{NH}_3$ vermiculite (fit 3)

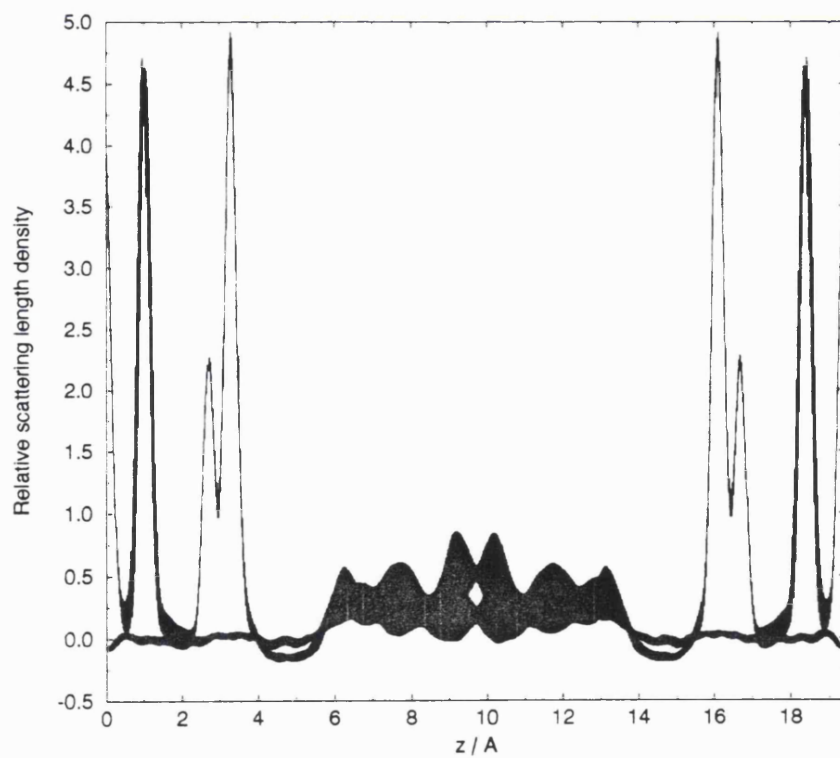


Figure 5.15d. Fitted density profiles for $\text{C}_4\text{H}_9\text{NH}_3$ and $\text{C}_4\text{D}_9\text{NH}_3$ vermiculite (fit 4)

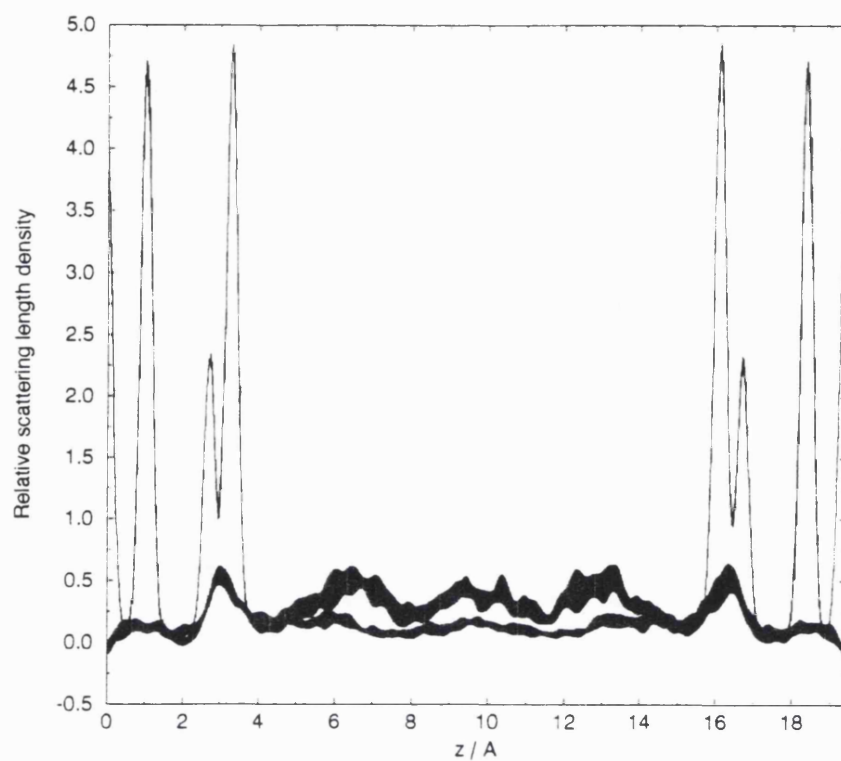


Figure 5.15e. Fitted density profiles for $\text{C}_4\text{H}_9\text{NH}_3$ and $\text{C}_4\text{H}_9\text{ND}_3$ vermiculite (fit 5)

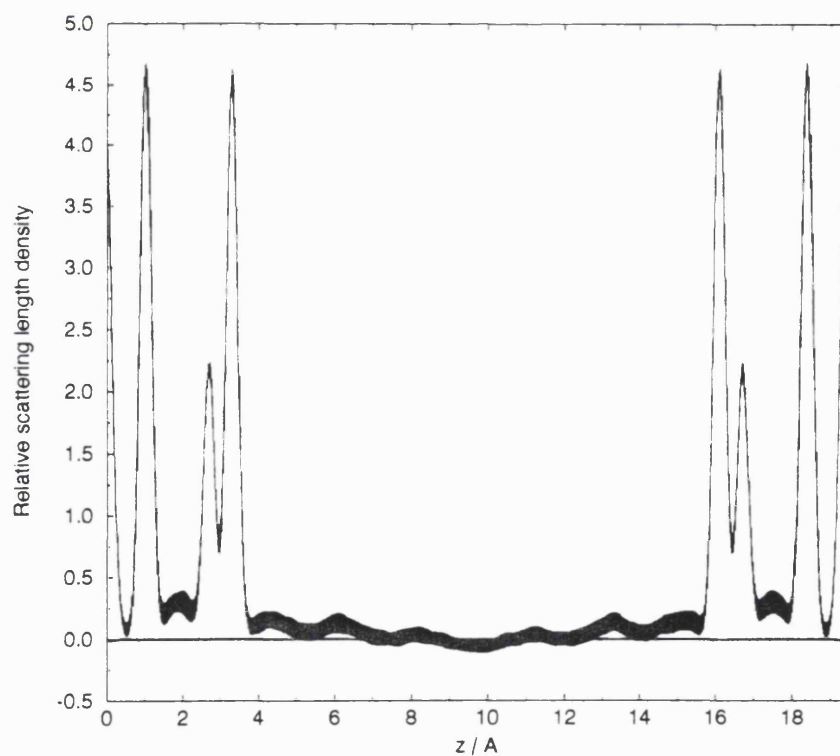
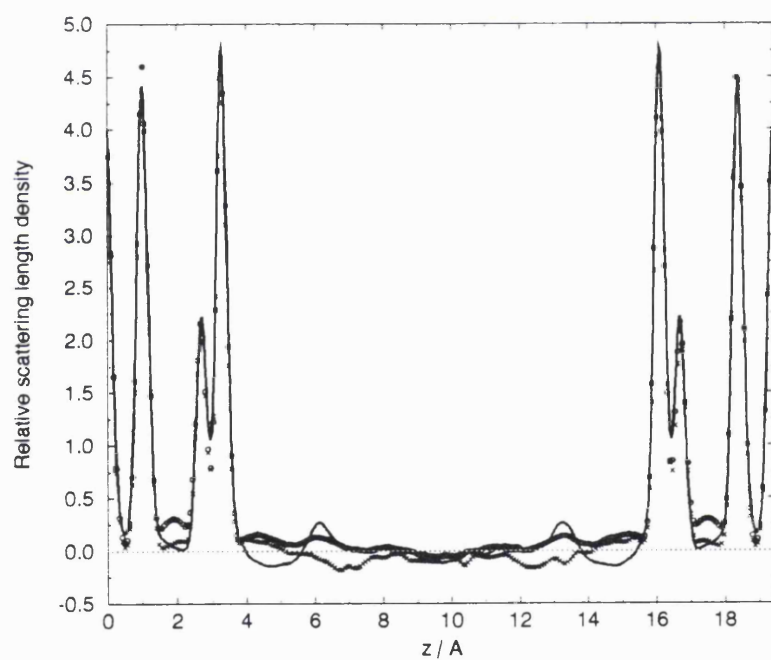
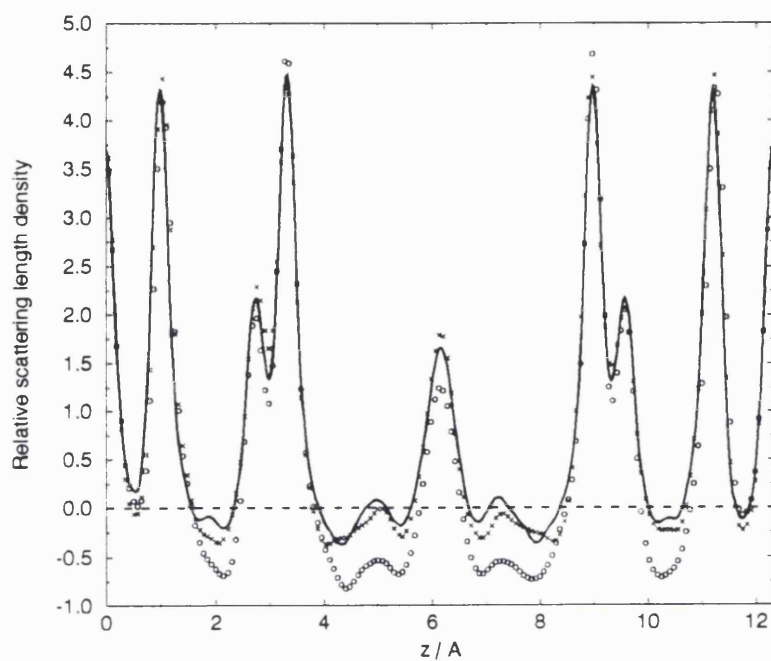


Figure 5.15f. Fitted density profiles for $\text{C}_4\text{H}_9\text{NH}_3$ and $\text{C}_4\text{H}_9^{15}\text{NH}_3$ vermiculite (fit 6)



Figures 5.16a and 5.16b. Comparison of the total fitted density profiles for isotopically unsubstituted MeNH_3 (top) and BuNH_3 (bottom) vermiculites. Profiles are constructed from the fits for substitution of alkyl H/D (line), $\text{H}_2\text{O}/\text{D}_2\text{O}$ (crosses) and $^{15}\text{N}/^{nat}\text{N}$ (circles).

5.12 Structural Interpretation

5.12.1 MeNH₃ Vermiculite

The main features of the three fits are as follows.

- 1) The difference profile representing the alkyl protons (figure 5.9) shows a broad peak at 6.15Å (at the centre of the interlayer), which extends out to ± 1.85 Å.
- 2) The H₂O / D₂O difference profile (figure 5.10) has a very broad peak covering the whole interlayer. The greatest intensity is located at 5.1 and 7.2Å, with a slight dip in the centre.
- 3) The ¹⁵N / ^{nat}N difference profile (figure 5.11) has a peak at 6.15Å. The nitrogen substitution represents only a very small change (~1%) of the total scattering from the sample, much less than for either of the H / D substitutions. As a result the magnitude of this peak is relatively close to the magnitude of features which are assumed to be due to errors in the data (figure 5.15c). This peak is however found to be consistent with the structure assigned on the basis of the other profiles.
- 4) The common profiles in all three fits have sharp peaks at 6.15Å and two much smaller humps at 5 and 7.3Å (figures 5.9 - 5.11).
- 5) In both the H₃/D₃ and H₂O/D₂O fits (figures 5.9 and 5.10) there is more (positive) intensity in the common components and less in the difference components than expected, regardless of the number of water molecules present. This is attributed to the presence of hydrogen of sample 4 and of deuterium in sample 1.

It is concluded that the ions sit on average in the centre of the interlayer with the C-N bond parallel to the clay surfaces. This is consistent with (3). Assuming that the CH₃ groups are free to rotate and that there is a range of angles between the C-N bond

and the clay layer then this is also consistent with (1). If the ions were perfectly ordered parallel to the sheets then the peak in the alkyl proton substitution profile would cover a region $2\text{\AA}$ in width, the length of the C-H bond being $1\text{\AA}$. In reality a single structureless peak is seen, with its maximum intensity at $6.15\text{\AA}$ and intensity out to $\pm 2\text{\AA}$. This indicates that some of the carbon atoms must be located at least $1\text{\AA}$ above and below the centre plane. This corresponds to a maximum angle of 50° between the mid plane and the C-N bond of the counterions.

The presence of excess salt in the clay crystals means that there will be a number of $\text{MeNH}_3^+ / \text{Cl}^-$ ion pairs in the interlayer. This quantity was measured (section 6.3) and the effective concentration of excess ion pairs inside the clay found to be 0.1M . As the effective counterion concentration in MeNH_3 vermiculite is $\sim 7\text{M}$ this represents a very small proportion of the total ($<2\%$) and so the excess salt is neglected in this assignment. This consideration applies equally in the case of BuNH_3 vermiculite.

This model is also consistent with the sharp peak at $6.15\text{\AA}$ in (4), which is attributed to carbon and nitrogen. Although both NH_3 and CH_3 scatter negatively the rotation of these groups spreads the negative component (i.e. the hydrogen atoms) over a greater length of the c^* axis, so leaving an overall positive component at the mid plane. If the ions are lying parallel to the surface (and again assuming free rotation) then the NH_3 groups will make a contribution to the $\text{H}_2\text{O} / \text{D}_2\text{O}$ difference profile that is identical to the H_3 / D_3 difference. Subtracting the latter from the former (figure 5.17) gives the location of the water protons, showing that there is layer of water molecules associated with each of the clay surfaces.

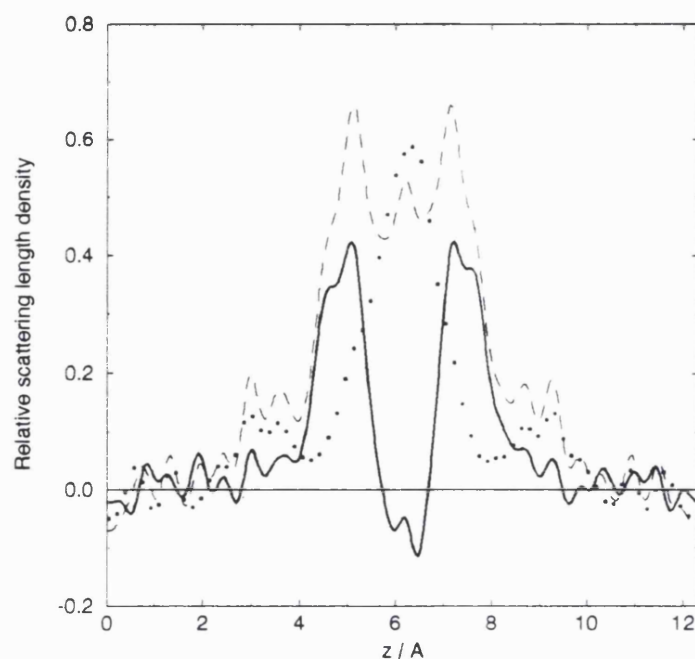


Figure 5.17. Plot of the difference profiles for fit 1 (filled circles) and fit 2 (dashed line). The difference between these (solid line) gives the location of the hydrogen atoms in the water molecules.

5.12.1 BuNH₃ Vermiculite

The main features of the three fits are as follows.

- 1) The difference profile representing the alkyl protons (figure 5.12) has a broad peak covering the whole region from 5.4 to 14.0 Å, with a maximum in the centre of the interlayer (9.7 Å). There are subsidiary peaks at 7.5 and 11.9 Å, although these are not very pronounced. The common profile for the same fit shows a broad peak over the same region with slight maxima at 6.2 and 13.2 Å, although these are found (figure 5.16b) to be inconsistent with the other fits.
- 2) The H₂O / D₂O difference profile (figure 5.13) covers the whole of the interlayer region and has three broad maxima at 6.5, 9.7 and 12.9 Å. It also has peaks in the clay layer region at 3.0 and 16.4 Å. The common profile for this fit is almost featureless, but shows slight maxima at positions corresponding to those in the substituted profile.

- 3) The $^{15}\text{N} / ^{\text{nat}}\text{N}$ difference profile (figure 5.14) has no significant features. This indicates that the difference in the data for the two samples was too small to fit. This was confirmed by running the fitting program to fit a difference between two (identical) data sets from the $^{\text{nat}}\text{N}$ sample. This produced an identical difference profile to that in figure 5.14. The common profile has no peaks, having instead a broad minimum across the whole interlayer, centred at $9.7\text{\AA}$.
- 4) All the total profiles for the natural sample (figure 5.16b) are rather featureless in the interlayer region.

It is more difficult to assign a detailed structure to the BuNH_3 system, because of the larger interlayer space and the greater number of structural possibilities with ions that have several rotational conformations. If anything there is rather less order than in the MeNH_3 system, as shown by the lack of any sharp interlayer features in any of the fits, either in the common or difference profiles.

The intensity in the alkyl proton difference profile is spread fairly evenly over $8.6\text{\AA}$. The maximum separation of the alkyl protons projected along the $\text{H}_3\text{C-C}$ bond is $4.7\text{\AA}$, along the C-N bond it is $3.8\text{\AA}$ and across the alkyl chain it is $3.0\text{\AA}$. This suggests that the ions lie in two layers with the C-N bond perpendicular to the clay surfaces and the NH_3 group directed towards one of the clay surfaces (i.e. with the alkyl chain at an angle of 54° to the clay surface, figure 3.4b), but that this ordering is sufficiently weak to average out any fine structure. Assuming the two layers were just in contact then the alkyl protons would be seen over a distance of $7.6\text{\AA}$ along the c^* axis, so there appears to be little interpenetration of the two layers of counterions. There is probably some tilting of the ions to a larger angle between the alkyl chain and the clay surface and/or dislocation of the ions away from the clay surface.

The difference peaks at 6.5 and 12.9Å in (2) are allocated to the NH₃ protons, suggesting that the peak at 9.7Å is due to water. There is therefore no evidence of segregation of the ions from the water, or of any pronounced water structure developing.

5.13 Conclusion

The MeNH_3^+ ions are found to lie principally parallel to the clay surfaces while the BuNH_3^+ ions sit perpendicular to the surface. This is consistent with the model presented in chapter 3, in which the size of the larger alkyl-ammonium counterions prevents them from lying parallel. The ordering appears to be stronger in the MeNH_3 vermiculite although this may partly reflect the greater difficulty of assigning a structure for BuNH_3 vermiculite, in which the clay layer spacing is greater and the ions have several rotational conformations. Both systems are relatively disordered compared to vermiculites containing more strongly hydrating counterions such as Li or Na. Also there is no evidence in either system of segregation of the alkyl groups from the water to form micelle like structures. In both systems the ions appear to be equally free to leave the clay surface and become fully hydrated, allowing the onset of macroscopic swelling. This experiment therefore shows no clear reason from the interlayer structure alone why butyl-ammonium vermiculite exhibits swelling behaviour while methyl-ammonium vermiculite does not. This is discussed fully in chapter 8.

Characterisation of Propyl-Ammonium Eucatex Vermiculite

6.1 Contents

This chapter describes experiments carried out to characterise PrNH_3 Eucatex vermiculite, which was found to be a suitable system for measurement of an electrical double layer structure. Two sets of experiments were carried out. Firstly, the layer spacings in the swollen gels were investigated by neutron diffraction as a function of salt concentration and temperature. Secondly, the Volhardt titration for chloride ions was used to measure the salt concentration both inside macroscopically swollen vermiculite gels (c_{int}) and in the soaking (supernatant) solution in contact with the gels (c_{ext}). These results were used to calculate the amount of salt trapped in the clay crystals and the ratio of the internal to external salt concentration. The two sets of experiments are described in sections 6.2 and 6.3 respectively.

6.2 Small Angle Neutron Scattering Studies

The layer spacings in the gels were investigated using small angle neutron scattering (SANS). Neutrons were used (as opposed to any other diffraction technique) for two reasons. Firstly, the available momentum transfer range allowed measurement of the (001) Bragg reflection (and so determination of the clay layer spacing) for vermiculite gels with clay layer spacings of up to $\sim 300\text{\AA}$, while the available X-ray diffraction facilities would only allow determination up to $\sim 50\text{\AA}$. Secondly, to remain in

equilibrium the gels must be kept in contact with the swelling solution in a sealed cell (to prevent evaporation). Because neutrons are very penetrating the presence of the cell does not unduly reduce the scattered intensity from the clay gel.

6.2.1 Sample Preparation and Container

Propyl-ammonium Eucatex crystals were prepared as described in section 5.2. Individual crystals were then weighed and placed in quartz cells, 10mm square by 40mm high. Crystals were selected with weights in the range 0.01 to 0.04g and placed in the sample cells with the clay layers horizontal (figure 6.1). A 1ml to 5ml adjustable pipette was used to add the necessary volume of PrNH_3Cl / D_2O solution to give a clay:water volume fraction of 0.01. The sample cells were then capped with Teflon lids and sealed with parafilm. Samples were prepared using solutions of ten concentrations : 0, 0.01, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5M. Because of possible sample to sample variation four samples were prepared at each concentration.

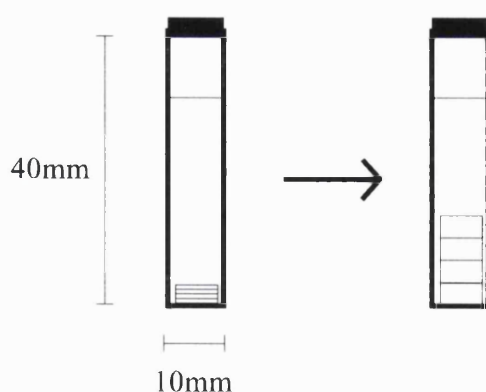


Figure 6.1. Side view of the 10mm square by 40mm high quartz cell. Clay crystals were placed in the cell as shown, with the clay layers horizontal (left). Solution was then added and the clay allowed to swell inside the cell (right).

The gels were prepared two weeks in advance to ensure that swelling had reached equilibrium before diffraction measurements were carried out, although the swelling appeared by eye to be complete within a couple of minutes. This is much faster than in the case of BuNH₃ Eucatex, which typically takes two or three days for apparent completion of macroscopic swelling (Mayne 1992).

6.2.2 The LOQ Diffractometer and Data Collection

The experiments were carried out on the LOQ diffractometer at the ISIS Facility, details of which can be found in *The LOQ Instrument Handbook* (King and Heenan 1996). The LOQ diffractometer (figure 6.2) uses a hydrogen moderator at 25K, producing neutrons with wavelengths in the range 2 - 12Å.

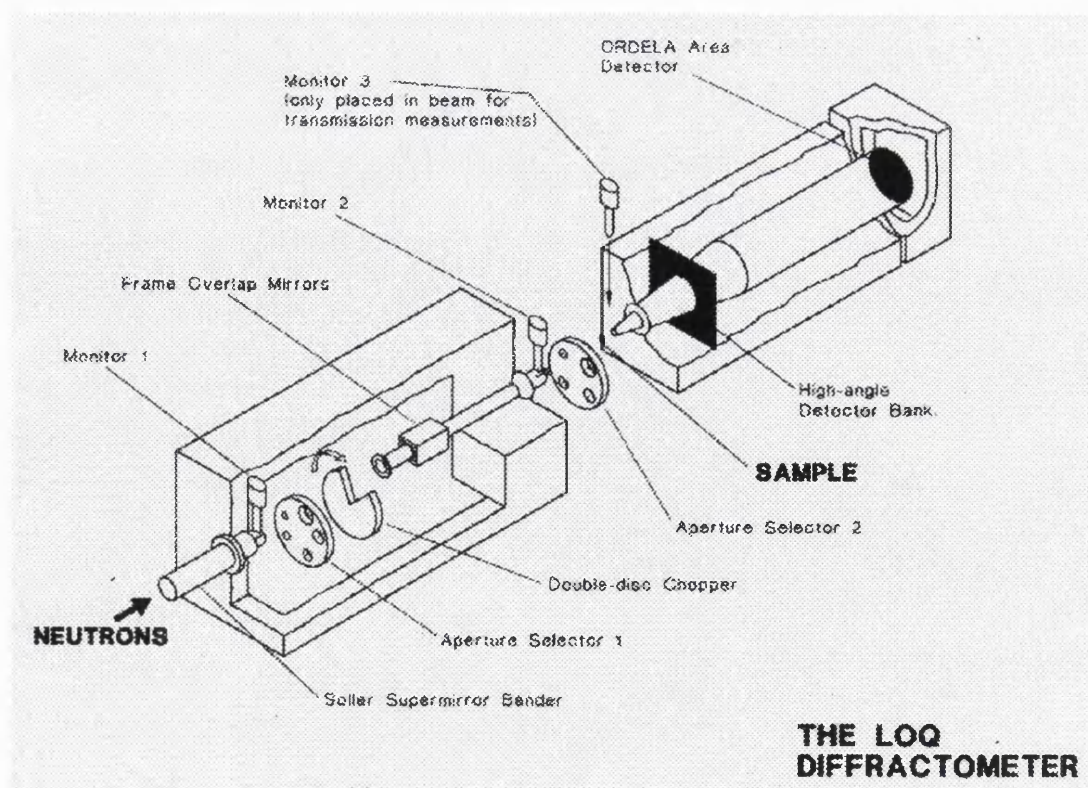


Figure 6.2. The LOQ Diffractometer (Source: ISIS Web Site)

The neutron beam was collimated and then defined by a slit, 2mm high by 8mm wide, the beam being horizontally incident on the sample cells. The cells were mounted with the clay layers horizontal and parallel to the beam, on a 20 position automatic sample changer. A laser reflected off a mirror placed in the line of the beam was used to locate the centre of the beam while aligning the samples. The temperature of the samples was controlled by a water bath connected to channels in the sample block, and was initially set at 280K.

A 64cm by 64cm position sensitive ^3He detector was used, giving a Q range of $0.006 - 0.23 \text{ \AA}^{-1}$. This is sufficient in practice to observe the (001) Bragg peak for gels with clay layer spacings up to $\sim 300\text{\AA}$. The detector records the data as a function of time-of-flight and of position on the detector, the momentum transfer for a given time-of-flight being determined by the radial distance from the detector centre. Because the gels are orientated most of the scattering occurs directly above and below the centre of the detector. The data were therefore summed only over the region within $\pm 30^\circ$ of the vertical axis of the detector.

Data were collected for each sample until the incident monitor had counted 10^6 neutrons, which took ~ 15 minutes. A transmission run for use in the data correction was also recorded for each sample, counting for ~ 3 minutes (2×10^5 neutrons). From each set of four samples the one showing the clearest (001) Bragg reflection was selected to investigate the temperature dependence of swelling. It had been observed while preparing the samples that the temperature at which the transition to the crystal phase took place (T_c) was above 290K for 0.5M samples and that this increased with decreasing salt concentration. The temperature was initially set to 292K and then measurements made at intervals of 2-4K, T_c being indicated by the disappearance of the (001) Bragg peak. In the available time measurements were made at temperatures up to

333K. This was sufficiently high to observe the phase transition for all except the 0M and 0.01M samples.

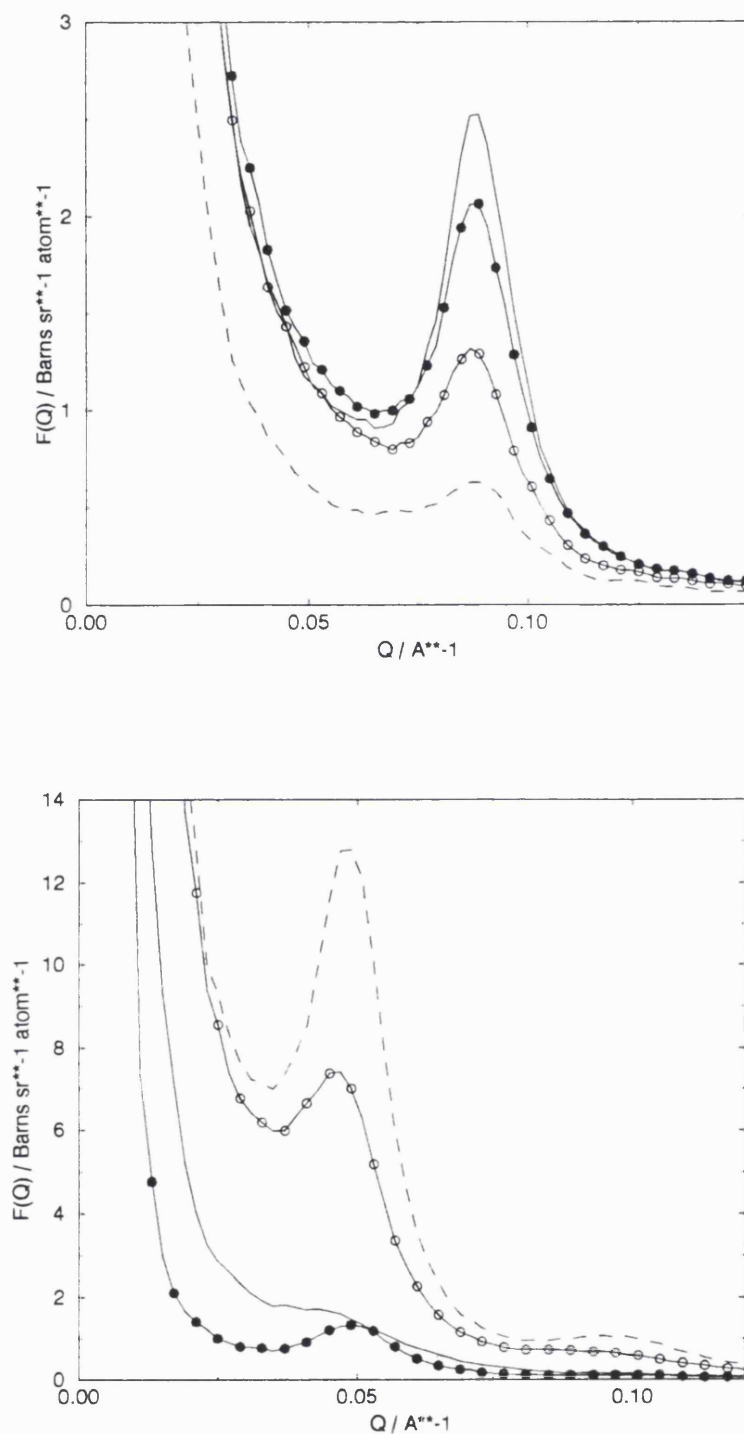
The data were interpreted by the position in Q space of the (001) Bragg peak and so did not require relative intensities, unlike the experiments described in chapters 5 and 7. It was found that this position was the same in the raw data as in the fully corrected DCS. Details of the standard correction procedure used are therefore omitted, but can be found in *Using Collette, A Simple Guide* (King 1997).

6.2.3 Results

For each sample the position of the (001) Bragg reflection was recorded, and the layer spacing of the gel calculated using the relation $Q = 2\pi / d$ (equation 4.11). Figures 6.3a and 6.3b show the corrected data for samples in 0.25M and 0.1M solutions, illustrating respectively the smallest and largest variation observed within a set of four samples. Table 6.1 gives the clay layer spacing at 280K for each sample as a function of concentration, showing the sample to sample variation as well as the average layer spacing. The average spacings are plotted as a function of salt concentration in figure 6.4.

The temperature at which transition to the crystal phase takes place was identified by the disappearance of the (001) Bragg peak. In most cases a sudden disappearance of the peak was observed (figure 6.5a) but for a few samples a residual shoulder was seen before its complete disappearance (figure 6.5b). In all samples a slight decrease in the layer spacing was observed before T_c was reached, illustrated by the slight shift in peak positions in figures 6.5a and 6.5b. Table 6.2 shows the layer spacing

as a function of temperature and concentration, with the transition temperature at each concentration.



Figures 6.3a and 6.3b. Plots of neutron scattering intensity for PrNH_3 vermiculite gels prepared in 0.25M (top figure) and 0.1M (lower figure) solutions of PrNH_3Cl , illustrating the possible variation in the (001) Bragg peak position and shape for different samples.

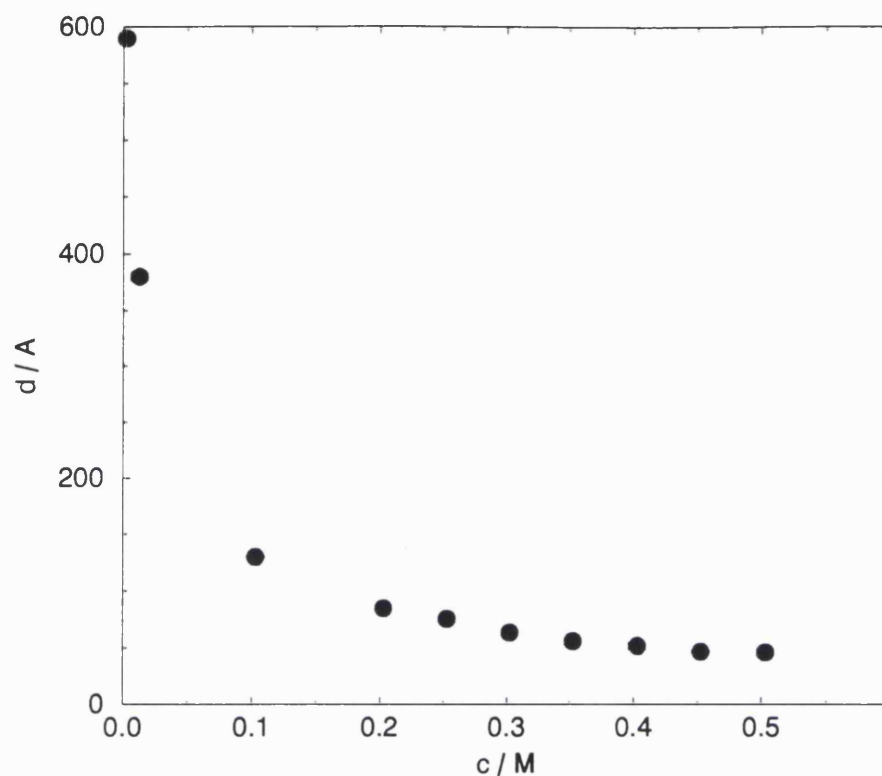
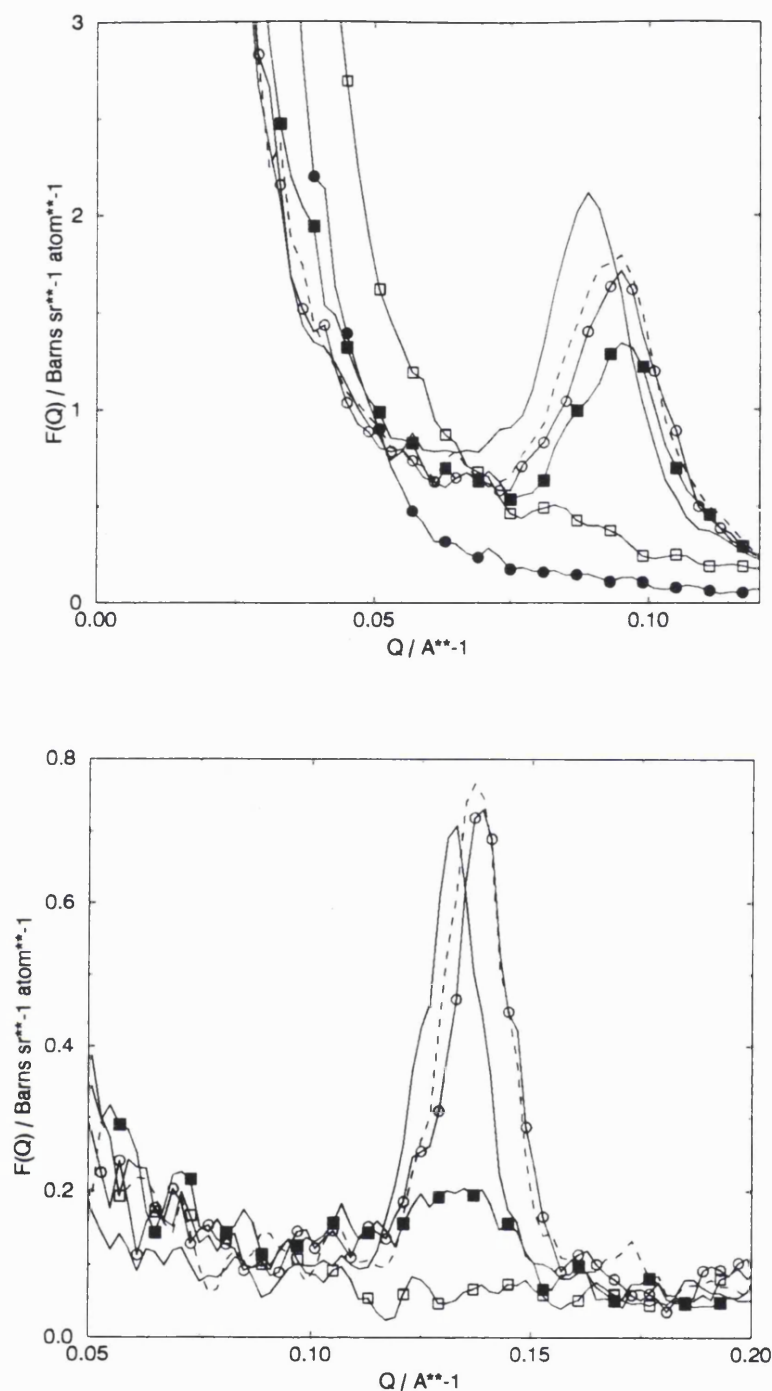


Figure 6.4. Graph of the average clay layer spacing as a function of salt concentration.

c / M	d_1	d_2	d_3	d_4	$d_{av} / \text{\AA}$
0.0	-	590	590	-	590
0.01	-	-	380	380	380
0.10	135	-	131*	127	131
0.20	-	86	84*	-	85
0.25	76	77*	76	77	76
0.30	65	64	63*	64	64
0.35	56*	57	-	56	56
0.40	52*	52	-	52	52
0.45	47*	-	48	47	47
0.50	47	45	46	45*	46

Table 6.1. Layer spacing in PrNH_3 Eucatex as a function of salt concentration, measured using the LOQ diffractometer. Results are given for all samples (with a dash indicating no observed Bragg peak) and the average spacing is shown in bold. '*' indicates the sample chosen to investigate the layer spacing as a function of temperature.



Figures 6.5a and 6.5b. Plots of neutron scattering intensity as a function of temperature for PrNH_3 vermiculite gels. The top figure is for a gel in 0.25M solution at 280K (solid line), 305K (dashed line), 308K (line with $\circ$), 312K (line with $\blacksquare$), 315K (line with $\square$) and 319K (line with $\bullet$). The lower figure is for a gel in 0.45M solution at 280K (solid line), 292K (dashed line), 295K (line with $\circ$), 299K (line with $\blacksquare$) and 302K (line with $\square$). Both illustrate the shift of the (001) Bragg peak to higher Q with increasing temperature. The lower figure also shows the partial disappearance of the peak near T_c (299K).

c / M	0.10	0.20	0.25	0.30	0.35	0.40	0.45	0.50
T / K								
280	131	84	77	63	56	52	47	45
292	-	-	-	-	-	50	46	45
295	-	-	-	60	54	50	45	X
299	-	-	-	60	53	49	X	X
302	-	-	67	59	52	48	X	-
305	-	-	65	58	52	X	X	-
308	-	79	65	59	X	X	-	-
312	126	77	63	X	X	-	-	-
315	121	75	X	X	-	-	-	-
319	121	X	X	-	-	-	-	-
322	121	X	-	-	-	-	-	-
326	121	-	-	-	-	-	-	-
330	121	-	-	-	-	-	-	-
333	X	-	-	-	-	-	-	-
T_c / K	332±2	317±2	314±2	310±2	307±2	303±2	299±3	293±2

Table 6.2. Clay layer spacings (Å), calculated from the (001) Bragg peak position, as a function of salt concentration (c) and temperature (T). ‘X’ indicates that no Bragg peak was seen; ‘-’ indicates that no measurement was made at that point. The final line gives the gel to crystal transition temperature (T_c) at each concentration.

6.2.4 Discussion

The results show that the swelling of PrNH₃ vermiculite is qualitatively similar to that of BuNH₃ vermiculite. The layer spacing is found to be proportional to $c^{-1/2}$ (figure 6.6). Macroscopically swollen PrNH₃ vermiculite gels therefore behave as typical one dimensional colloids, whose behaviour can be described at relatively large particle separations by theories based on primitive electrostatic models such as that of Sogami (Sogami and Ise 1984). They are therefore an ideal system in which to investigate the assumptions made in the primitive model.

The gel to crystal transition temperature is found to be inversely proportional to $\log c$ (figure 6.7), as for BuNH₃ vermiculite swelling. At a given concentration however T_c is higher in PrNH₃ vermiculite, and the rate of change of T_c with concentration is also greater for PrNH₃ vermiculite. PrNH₃ vermiculite therefore exhibits swelling in higher salt concentrations and the gel phase can be prepared with a smaller clay layer spacing, down to $\sim 40\text{\AA}$. This is a crucial advantage for determining the double layer structure in PrNH₃ vermiculite, as it can be prepared as a colloidal system with a sufficiently small particle separation for measurement of the (001) Bragg reflection using the LAD diffractometer. The differences between the swelling behaviour of the two systems also indicate the limitations of the primitive model in describing such systems: the higher transition temperatures exhibited by PrNH₃ vermiculite could be attributed to the lower entropic cost of hydration of the alkyl groups. This is discussed in chapter 8.

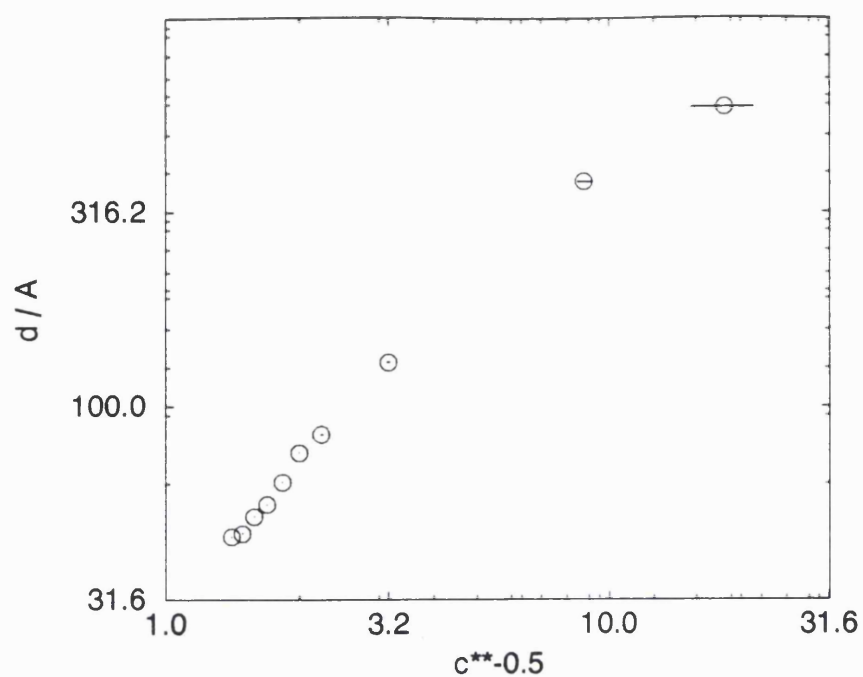


Figure 6.6. Graph of clay layer spacing (d) as a function of salt concentration (c). The layer spacing is observed to increase in proportion to $c^{-1/2}$.

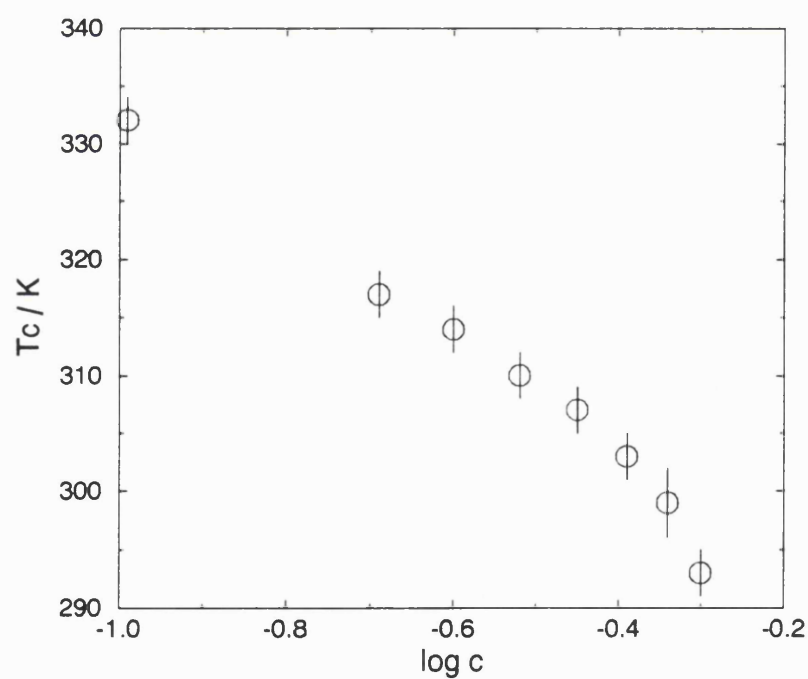


Figure 6.7. Graph of the gel to crystal phase transition temperature (T_c) as a function of salt concentration (c). T_c is observed to decrease in proportion to $\log c$.

6.3 Determination of the Salt Fractionation Ratio and Trapped Salt Concentration

To determine the actual salt concentration in the clay/soaking solution system it is necessary to know two quantities: i) the salt fractionation ratio (S_R) is the ratio of the salt concentration in the solution around a gel to the concentration of salt present inside a gel (not including the counterions); ii) the trapped salt concentration (c_{tr}) is the amount of excess salt present inside the clay crystals.

Both of these can be determined by the Volhardt titration (Treadwell and Hall 1919) for chloride ions, using the following procedure. A measured volume of clay crystals are swollen in a known volume of solution of a known concentration; after swelling is complete the supernatant fluid is removed and weighed to find the volume which has been absorbed by the vermiculite; the absorbed fluid is extracted from the gel; the salt concentrations in both the supernatant fluid and fluid extracted from the gel are determined by the Volhardt titration. The ratio of these concentrations gives the salt fractionation ratio, while the total salt content of the system gives the trapped salt concentration.

6.3.1 The Volhardt Titration

- (1) $\text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{AgCl}$ (white precipitate)
- (2) $\text{Ag}^+ (\text{aq}) + \text{SCN}^- (\text{aq}) \rightarrow \text{AgSCN}$ (white precipitate)
- (3) $4 \text{SCN}^- + \text{Fe}^{3+} \rightarrow \text{Fe}(\text{SCN})_4^- (\text{aq})$ (blood red colour)

The Volhardt titration for chloride ions involves precipitation of Cl^- with silver nitrate (1), followed by a back titration of the excess Ag^+ using potassium thiocyanate (2) in the presence of an acidified iron (III) nitrate indicator. The end point is indicated

by the blood red colour of the iron thiocyanate complex formed by free thiocyanate ions

(3). The concentration of chloride ions in a sample is then given by

$$[\text{Cl}] = (V_{\text{Ag}} [\text{Ag}] - V_{\text{SCN}} [\text{SCN}]) / V_{\text{Cl}} \quad (6.1)$$

where V_X and $[X]$ represent, respectively, the volume and concentration of species X.

This method can be used to measure chloride concentrations as low as 0.005M, although at lower concentrations the end point becomes difficult to identify accurately.

6.3.2 Experimental Procedure

Samples were prepared as follows. PrNH_3 Eucatex crystals (exchanged as described in 5.2) were weighed into a 10ml sample jar and solutions of PrNH_3Cl (aq) of various concentrations added from an adjustable pipette to give a known clay:water volume fraction. The density of the clay crystals was calculated, as there was insufficient sample available for an accurate experimental determination. This calculation was done on the basis of the experimentally determined density of 1.86 gcm^{-3} for BuNH_3 crystals (Moody 1992), assuming the water content to be the same in each case. The calculated density was 1.90 gcm^{-3} . A typical sample contained $\sim 0.2\text{g}$ of clay and $\sim 5\text{cm}^3$ of solution.

Samples were prepared with four different concentrations (c) and volume fractions (r). Three sets of ten samples were prepared with $r = 0.02$ and $c = 0\text{M}$, 0.02M and 0.1M in order to investigate the salt fractionation ratio as a function of added salt concentration. Two samples were also prepared under the conditions ($r = 0.07$, $c = 0.5\text{M}$) of the samples used to measure the electrical double layer structure (chapter 7). The jars were then sealed with parafilm and weighed. The jars were weighed again after swelling was complete to ensure that no fluid had evaporated during the swelling process.

The samples were left for 10 days to ensure that swelling was complete and that the gels were in equilibrium with the supernatant solution. The supernatant solution was then removed using a Pasteur pipette, as quickly as possible to minimise any re-equilibration while the supernatant solution was being removed from the gel. This typically took twenty to forty seconds to complete, while it was observed that fluid began to escape from some of the 'bare' gels after ~5 minutes. The supernatant solution was weighed and hence the fraction of the solution absorbed by the clay calculated.

After removal of the supernatant solution a small quantity of KHCO_3 crystals were sprinkled on the gels, causing a transition to the crystalline phase as diffusion of K^+ ions into the interlayer region took place (Williams et al 1994). This allowed the fluid absorbed by the gel to be removed for titration, without changing its chloride ion concentration.

For each sample, portions of both the internal and supernatant solutions were titrated using the Volhardt titration. Solutions of AgNO_3 (aq) were prepared with concentrations of 0.1M and 0.01M; solutions of KCNS (aq) with concentrations of 0.05M and 0.005M. Measured volumes of the sample and AgNO_3 solution were placed together in a conical flask using an adjustable pipette and ten drops of conc. HNO_3 / $\text{Fe}(\text{NO}_3)_3$ indicator added. A solution of KCNS was then added from a burette until the red colour indicating the end point was observed. Two portions of each sample were titrated to ensure the consistency of the results, and concentrations calculated from the average of the two results using equation 6.1. The concentrations and volumes used in each case (table 6.3) were selected to optimise the accuracy of the titrations, the limiting factors being the volume of sample available and the increasing difficulty of locating the end point as the solution becomes more dilute.

Sample	c / M	r	$[\text{Ag}] / \text{M}$	$V_{\text{Ag}} / \text{cm}^3$	$[\text{KCNS}] / \text{M}$	$V_{\text{sample}} / \text{cm}^3$
1 - 10	0.00	0.02	0.01	3.05	0.0049	0.99
			0.01	1.05	0.0049	0.395
11 - 20	0.02	0.02	0.1	0.995	0.0049	1.55
			0.01	2.05	0.0049	0.295
21 - 30	0.10	0.02	0.1	3.05	0.049	1.55
			0.01	2.05	0.0049	0.295
31 - 32	0.50	0.07	0.1	8.1	0.049	1.01
			0.1	1.05	0.049	0.195

Table 6.3. Volumes and concentrations of the AgNO_3 and KCNS solutions used for each set of Volhard titrations. These were selected to minimise the errors in each case. Two rows of numbers are shown for each sample set, the first representing titrations on the supernatant solutions and the second on solutions extracted from the gels. The values given have been corrected using the calibrations described below.

Prior to titration of the samples three calibrations were carried out. The two adjustable pipettes used were calibrated by weighing samples of demineralised water over the range of volume settings used, assuming a density for water of 1gcm^{-3} . The smaller pipette (50-500 μl in volume) was found to give 5 μl less than the set amount, while the larger (1-5ml in volume) gave 0.05ml more than the set amount. Both of these deviations were found to be independent of the volume setting on the pipette. The volumes shown in table 6.3 are corrected accordingly.

The concentrations of the solutions of AgNO_3 and KCNS were calibrated by titrations using all four possible combinations of concentrations. In each case the titre was found to be 2% over the expected value. As this effect was consistent for all solutions it was probably due to over titration as a result of the difficulty of seeing the end point. This was corrected for by taking the concentrations of the KCNS solutions to be 2% less than their actual values (table 6.3).

Finally titrations were carried out in which a small quantity of KHCO_3 had been added, and it was verified that this did not alter the outcome of the titration.

6.3.3 Results

Table 6.4 lists, for each sample: the volume of fluid absorbed by the clay, expressed as a fraction of the total volume of solution; the chloride concentration in the supernatant solution (c_{ext}); the chloride concentration inside the gel (c_{int}). Average values were calculated for each set of conditions. These were used to calculate the following quantities, the results being listed in table 6.5.

i) the clay layer spacing in the gel. This was calculated, assuming that there is no density change in solution absorbed by the clay, by multiplying the crystal spacing of $18.6\text{\AA}$ by the number of volume equivalents of water absorbed by the clay.

ii) the salt fractionation ratio, $c_{\text{ext}} / c_{\text{int}}$.

iii) the concentration of salt trapped in the original crystals (c_{tr}). This was obtained by calculating the total salt content of the system and subtracting the added salt, and is given in moles per litre of clay.

Sample No.	Fraction abs.	c_{ext}	c_{int}	$c_{\text{ext}} / c_{\text{int}}$ (r, c)
1	0.47	0.0058	0.0030	$c = 0\text{M}$ $r = 0.02$
2	0.46	0.0070	0.0043	
3	0.45	0.0068	0.0036	
4	0.48	0.0051	0.0024	
5	0.45	0.0068	0.0049	
6	0.47	0.0073	0.0049	
7	0.41	0.0070	0.0036	
8	0.49	0.0068	0.0049	
9	0.47	0.0061	0.0043	
10	0.50	0.0058	0.0024	
	0.46 $\pm$ 0.02	0.006 $\pm$ 0.001	0.004 $\pm$ 0.001	1.5 $\pm$ 0.5
11	0.29	0.028	-	$c = 0.02\text{M}$ $r = 0.02$
12	0.29	0.026	0.017	
13	0.31	0.026	0.016	
14	-	0.025	0.015	
15	0.29	0.025	0.016	
16	0.27	0.025	0.015	
17	0.33	0.025	0.016	
18	0.31	0.027	0.016	
19	-	0.026	0.016	
20	0.31	0.026	0.016	
	0.30 $\pm$ 0.03	0.026 $\pm$ 0.001	0.016 $\pm$ 0.001	1.6 $\pm$ 0.2
21	0.19	0.116	0.057	$c = 0.1\text{M}$ $r = 0.02$
22	0.18	0.117	0.060	
23	0.18	0.112	0.064	
24	0.19	0.107	0.059	
25	0.19	0.104	0.062	
26	0.18	0.105	0.062	
27	0.18	0.107	0.059	
28	0.20	0.105	0.066	
29	0.18	0.107	0.062	
30	0.18	0.105	0.061	
	0.19 $\pm$ 0.01	0.108 $\pm$ 0.004	0.062 $\pm$ 0.003	1.7 $\pm$ 0.2
31	0.18	0.529	0.363	$c = 0.5\text{M}$ $r = 0.07$
32	0.20	0.536	0.341	
	0.19 $\pm$ 0.01	0.53 $\pm$ 0.005	0.35 $\pm$ 0.03	1.5 $\pm$ 0.05

Table 6.4. Results of titrations on PrNH_3 vermiculite gels, showing the fraction (by weight) of the solution absorbed by the clay and the external and internal salt concentrations. A dash indicates no successful titration. The average value for each set of samples is shown in bold. The final column gives the salt fractionation ratio and the r, c conditions of each sample set.

r	c	$d / \text{\AA}$	$c_{\text{ext}} / \text{M}$	$c_{\text{int}} / \text{M}$	$c_{\text{ext}} / c_{\text{int}}$	c_{tr} / M
0.02	0	450 ± 20	0.006	0.004	1.5 ± 0.5	0.25
0.02	0.02	300 ± 30	0.026	0.016	1.6 ± 0.2	0.15
0.02	0.1	200 ± 10	0.108	0.062	1.7 ± 0.2	-0.04(!)
0.07	0.5	68 ± 3	0.53	0.35	1.5 ± 0.1	-0.06(!)

Table 6.5. Average clay layer spacings and internal/external salt concentrations as a function of (r,c) .

6.3.4 Discussion

Although the Volhardt titration is useful there are a number of competing limitations on the degree of accuracy obtainable. The most important of these was the limited amount of clay crystals available. This meant that the volume of liquid available for titration was very small, in some cases only 0.2cm^3 . This was a particular problem for samples prepared in high salt concentrations, in which the clay absorbs only a very small quantity of solution. As the salt concentration is decreased the titration of the internal solution becomes more accurate because the gels absorb more solution and so more is available for titration. On the other hand the solutions become more dilute, so the total chloride content in the titration is still small, and for very dilute solutions it is difficult to see the end point. The variation between samples is found to be $\sim 1\text{-}10\%$ (table 6.4), which is relatively small compared to previous measurements on BuNH_3 vermiculites which have shown that there can be up to 10% sample to sample variation

(Williams 1993). Table 6.5 however indicates the presence of more serious systematic errors in the data.

Calculation of the trapped salt concentration, which must be independent of the added concentration, gives values which decrease as c is increased and even become negative for the 0.1M and 0.5M samples! This is not so dreadful as it appears however, as at these concentrations the added salt is only a small fraction (2-4%) of the total so these numbers are very inaccurate, being a small difference between two large numbers. The value most accurately representing c_{tr} was therefore taken to be that from the 0M samples, so

$$c_{tr} = 0.25 \pm 0.05M$$

Crystals of BuNH₃ vermiculite which have been washed twenty times in water at ~80°C were found to have a trapped salt concentration of $0.1 \pm 0.05M$ (Williams 1993). This washing procedure is not possible with PrNH₃ vermiculite as swelling would occur. Comparing these results suggests that the 60% of the excess salt in the PrNH₃ vermiculite crystals is present on the surface, while 40% occurs inside the interlayer itself.

The salt fractionation ratio appears to be independent of salt concentration, the values obtained being in the range 1.6 ± 0.1 . Similar measurements on BuNH₃ vermiculite (Williams 1993) found no systematic trend in the salt fractionation ratio as a function of salt concentration, values of S_R being found in the range ~1.5 to ~3.5.

There might however be a systematic error present in these results. Comparing the calculated layer spacings with those obtained by neutron diffraction (table 6.1) it is seen that for the 0.1 and 0.5M samples this method produces a value which is

significantly larger than the microscopically measured layer spacing. The most likely reason for this is the difficulty of removing all of the solution from around the gels, as each sample consists of many small pieces of clay (a single clay gel would not contain enough solution for titration). This effect will lead to an overestimate of the volume of solution absorbed. The idea is supported another observation: the measurements suggested that the 0.5M gels should contain $\sim 1.2\text{cm}^3$ of solution, while it was subsequently found to be impossible to remove more than 0.3cm^3 for use in the titrations.

This will increase the measured values of c_{int} , as the absorbed solution mixes with the (more concentrated) residual supernatant solution before the titration takes place. Furthermore the effect is concentration dependant: the volume of residual supernatant solution is independent of salt concentration, while the volume of absorbed solution decreases as the salt concentration is increased. At higher concentrations the two volumes are comparable and so the effect is more pronounced. The clay layer spacings measured by neutron diffraction are $130\text{\AA}$ and $45\text{\AA}$ in 0.1M and 0.5M solutions, while the values given by weighing the gels are $\sim 200\text{\AA}$ and $70\text{\AA}$ respectively. The inconsistencies between the two results for the layer spacings are therefore $70\text{\AA}$ and $25\text{\AA}$ respectively. If these inconsistencies are taken to represent the volume of residual external solution, then the actual values of c_{int} are 0.033M and 0.17M for the 0.1M and 0.5M samples respectively. The salt fractionation ratios then become 3.3 and 3.1 respectively. For the purposes of the experiments described in chapter 7 the salt fractionation ratio is therefore assumed to be ~ 3 .

Electrical Double Layer Structure in a Propyl-Ammonium Vermiculite Gel

7.1 Contents

This chapter describes experiments carried out to determine the electrical double layer structure in a macroscopically swollen propyl-ammonium vermiculite gel. These were carried out using the LAD Diffractometer at the ISIS Facility. Gels of two isotopic compositions were used containing $\text{C}_3\text{H}_7\text{ND}_3^+ / \text{D}_2\text{O}$ (sample 1) and $\text{C}_3\text{D}_7\text{ND}_3^+ / \text{D}_2\text{O}$ (sample 2) in order to locate the alkyl groups of the counterions. A third sample had been prepared containing $\text{C}_3\text{H}_7\text{NH}_3^+ / \text{H}_2\text{O}$ but it was not used because problems with the detectors on LAD led to loss of available beam time. The method used was similar to the one described in chapter 5, but with several significant differences. The experimental section in this chapter concentrates on these differences, the reader being referred where necessary to the appropriate section of chapter 5 for a full description. The results and their interpretation are then presented.

7.2 Sample Preparation and Container

PrNH_3 Eucatex crystals were prepared by exchanging Na Eucatex crystals in a 1M solution of $\text{C}_3\text{H}_7\text{NH}_3\text{Cl}$ (aq) (sections 5.2 and 5.3). Twenty of these crystals were placed in $\sim 50\text{cm}^3$ of a 0.5M solution of $\text{C}_3\text{H}_7\text{NH}_3\text{Cl}$ in H_2O and allowed to swell. The solution was replaced after 48hrs with $\sim 50\text{cm}^3$ of a 0.5M solution of $\text{C}_3\text{H}_7\text{ND}_3\text{Cl}$ in

D₂O, which was replaced with an identical 50cm³ portion after a further 24hrs. This repeated exchange of the swelling solution was necessary to remove the excess salt trapped in the crystals, which could otherwise have had an unpredictable effect on the clay layer spacing (sections 3.4.1 and 6.3). A significant difference between the layer spacings of two samples would make it very difficult to fit an isotopic difference profile.

The gels were left in the soaking solution for 5 days to ensure they had reached equilibrium. X-ray diffraction was then used to measure the layer spacing of a random selection of five of the gels, which was consistently $39.8 \pm 0.2\text{\AA}$. The gels were then removed from the soaking solution and put into a flat plate sample can (figure 7.1). This was made from a TiZr alloy which produces almost no coherent scattering, taking advantage of the opposite signs of the coherent neutron scattering lengths of Ti and Zr. The internal dimensions of the can were 55mm high by 19mm long by 2mm wide, the external dimensions being 23mm long by 4mm wide. A rectangular Teflon block 20mm high by 18mm long was placed in the bottom of the sample can, reducing the effective depth of the can and so easing the placement of individual gels into the can.

Gels were placed in the sample can with the clay layers parallel to the 19mm x 55mm faces of the cell (figure 7.2a). In order to ensure that the sample remained in this orientation individual gels were selected which were ~2mm thick. Six gels were used, of suitable dimensions to pack together as efficiently as possible and so maximise coverage of the neutron beam (figure 7.2b). A 0.5M solution of C₃H₇NH₃Cl in D₂O was then added, giving a volume fraction of 0.07. The presence of the solution was necessary to ensure that the gels remained in equilibrium, but meant that scattering measurements had to be made for the solutions in order to fully correct the data. The sample can was sealed with a stainless steel cap (figure 7.1) containing a Teflon washer and mounted on

a He gas closed cycle refrigerator. This maintained the sample at a temperature of 277K and so ensured that the transition to the crystal phase did not occur.

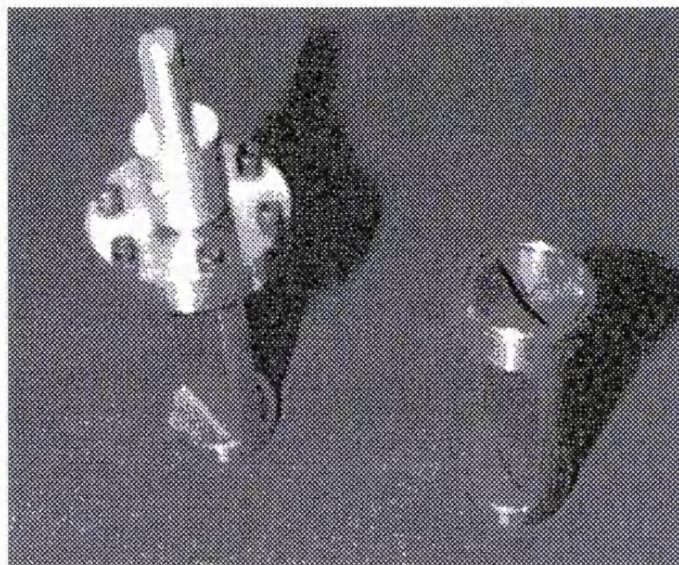


Figure 7.1. Picture of the TiZr sample can with and without the lid.

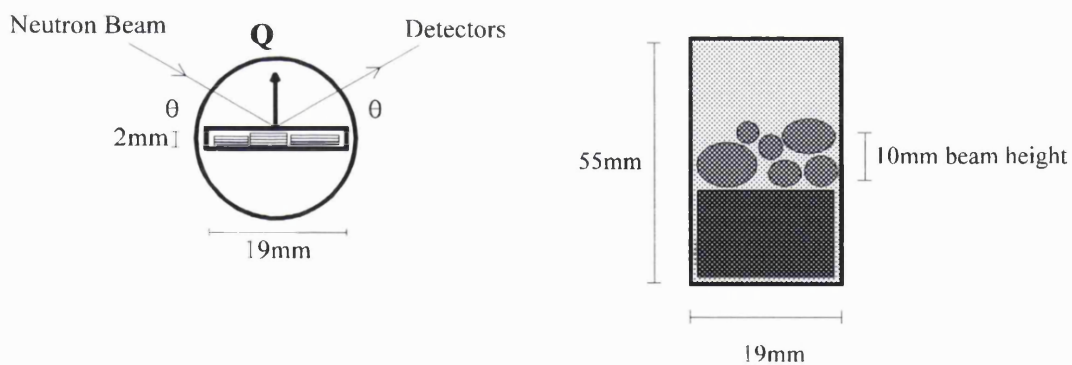


Figure 7.2a and 7.2b. Two schematic views of the gels in the TiZr can. The left hand figure is a plan view showing the gels orientated with the clay layers parallel to the long axis of the can and the orientation of the can relative to the neutron beam. The right hand figure is a side view showing how the Teflon spacer (dark grey), gels (grey) and solution (light grey) were arranged in the can.

7.3 Data Collection

The experiments were carried out on the LAD Diffractometer with the sample aligned to measure the (00 l) Bragg reflections (section 5.4). Data were collected for three sample orientations, scattering into detector banks at $2\theta = 5^\circ$, 35° and 150° . This allowed measurement of $F(Q)$ over the whole Q range available on LAD, from $50\text{\AA}^{-1}$ down to $0.07\text{\AA}^{-1}$, sufficiently low to observe the (001) Bragg reflection. For each orientation a rocking curve was measured (section 5.4) and the sample can rotated to maximise the measured intensities.

After data had been collected for the hydrogenated sample (sample 1) in all three orientations the solution was removed from the can using a syringe. The needle was carefully pushed down one edge of the sample can to avoid disturbing the clay gels. The solution was then replaced by an equivalent volume of 0.5M solution of $\text{C}_3\text{D}_7\text{NH}_3\text{Cl}$ in D_2O , this procedure being repeated four times at $2\frac{1}{2}$ hour intervals. Assuming exchange of ions between the gel and the solution to have reached equilibrium within $2\frac{1}{2}$ hours (MV Smalley, unpublished results) then the counterions in the gel were expected to be 90% deuterated. This method of substituting the counterions *in situ* had the important advantage that only one set of clay crystals were used and so errors due to variations between the samples were minimised. This had not been possible in the experiments on crystalline vermiculites, where exchange of the counterions is much slower due to the smaller distance between the clay layers.

While the sample was exchanging, data were collected for an empty can in all three orientations, for the empty instrument (background) and for a 3mm thick vanadium slab. Data were then collected for the deuterated sample and finally for the sample can containing solutions of i) 0.5M $\text{C}_3\text{H}_7\text{NH}_3\text{Cl}$ in D_2O (sample 3), and ii) 0.5M

$\text{C}_3\text{D}_7\text{NH}_3\text{Cl}$ in D_2O (sample 4), measurements again being made for all three orientations.

7.4 Data Correction

The sequence of corrections applied to obtain $F(Q)$ for the two gels is shown in figure 7.3. The basic sequence is the same as that given in section 5.5, but with several additional steps. This section outlines these and identifies possible sources of error in the procedure.

7.4.1 Joining The Data Sets

Unlike the data collected for the crystalline vermiculites the Bragg peaks were only individually resolved for $Q < 0.5 \text{ \AA}^{-1}$ (figure 7.4) and so discrete integrated Bragg intensities could not be obtained as described in section 5.6. It was therefore desirable to merge the data sets collected at different scattering angles to give the total structure factor over the whole Q range. The corrected data sets collected at $2\theta = 5^\circ$ and 35° were joined at $Q = 1 \text{ \AA}^{-1}$, after ensuring that the data were consistent over the whole region in which they overlapped (figure 7.5). The 150° data sets were not used because they contained a very large inelastic component (figure 7.6). While this could possibly have been removed by fitting it was decided that this was not worthwhile as i) this would not be very accurate, and ii) all the differences observed in the data due to isotope substitution were in the Q range covered by the 5° and 35° data sets.

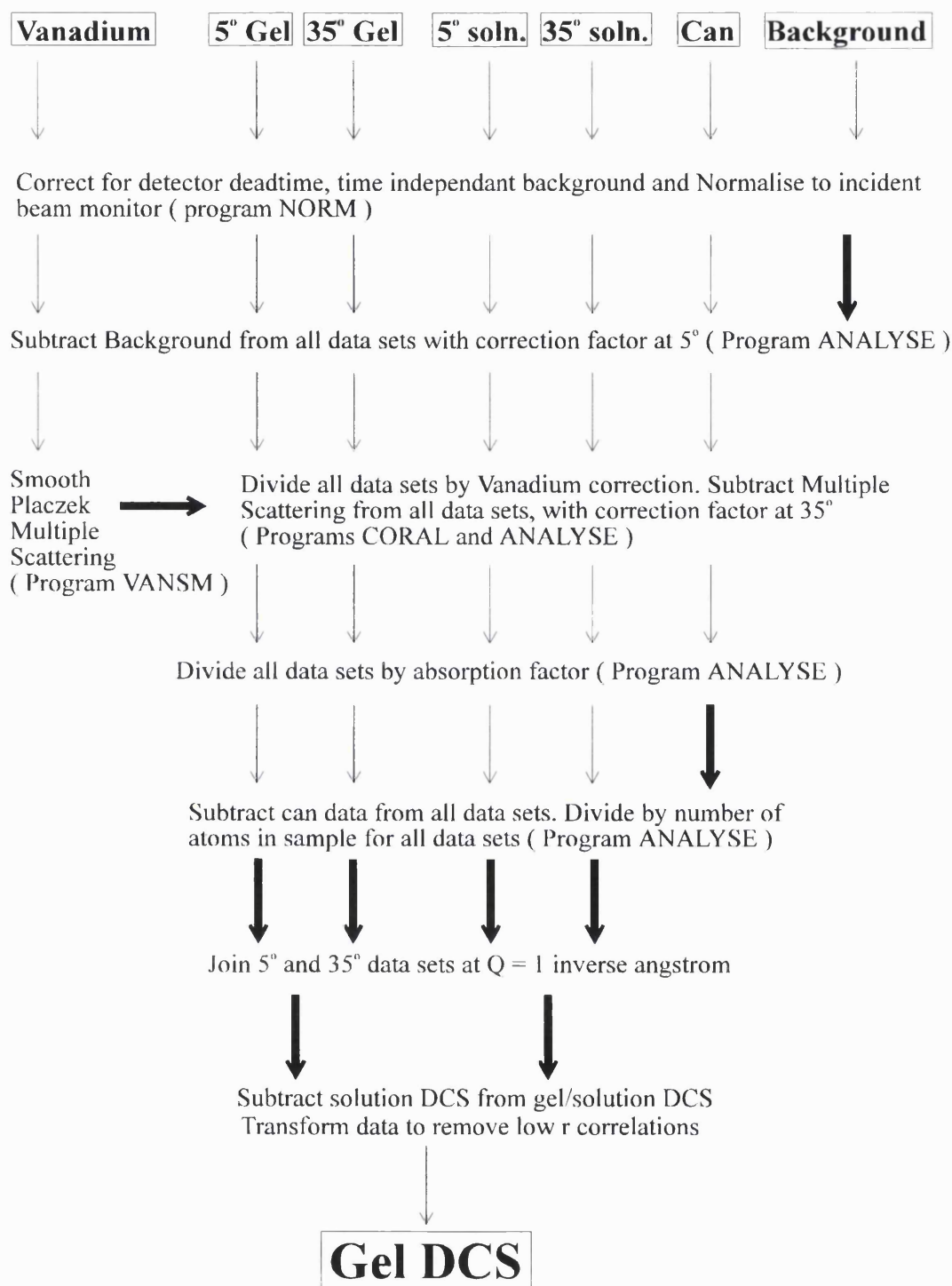


Figure 7.3. Sequence of corrections applied to obtain the sample differential cross section from the raw data. Boxed text refers to the data, unboxed text to operations applied to the data. Where arrows are shown in parallel this indicates that the operation below is applied to each data set in parallel; a bold arrow indicates that a data set is incorporated into the others in that operation.

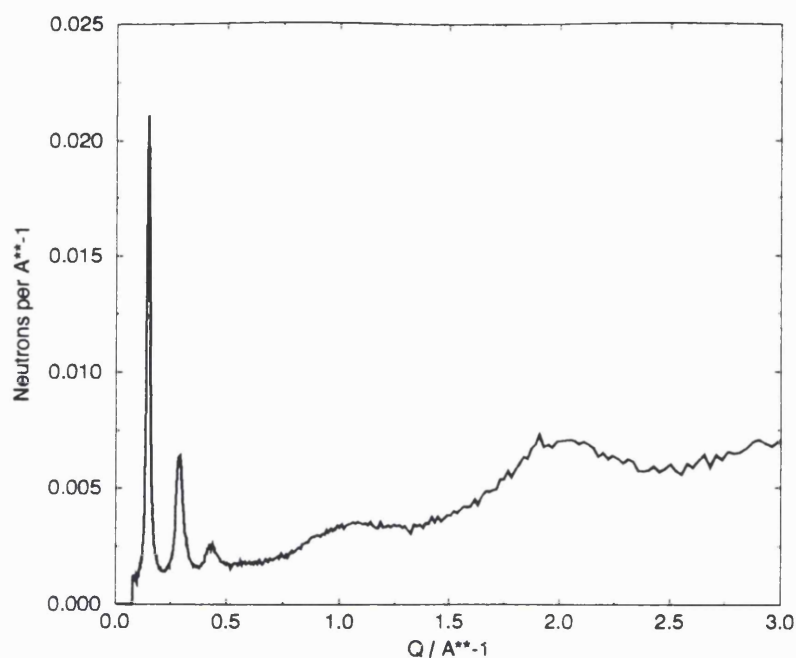


Figure 7.4. Data collected at $2\theta = 5^\circ$ for the $\text{C}_3\text{D}_7\text{ND}_3$ vermiculite gel, corrected for detector deadtime, time independent background and normalised to the neutron wavelength spectrum. This shows the presence of both individually resolved Bragg peaks and broad features.

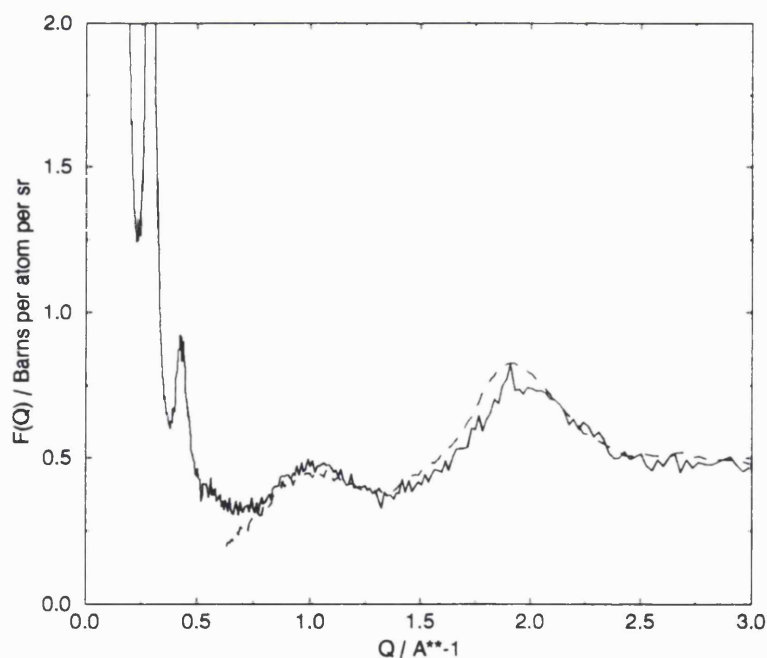


Figure 7.5. The total structure factor for the $\text{C}_3\text{D}_7\text{ND}_3$ vermiculite gel, measured at $2\theta = 5^\circ$ (solid line) and $2\theta = 35^\circ$ (dashed line). These show good agreement in the overlap region.

7.4.2 Correction for Solution in The Beam

The data sets had to be corrected for scattering from supernatant solution in the beam. The solution data were corrected in an identical manner to the gel data (figure 7.3) to give $F(Q)$ for each solution ($F(Q)_{\text{solution}}$). A fraction of these data sets corresponding to the fraction by volume of solution in the beam was then subtracted from the sample data to give $F(Q)$ for the gel ($F(Q)_{\text{gel}}$). This fraction was determined while removing the solution from the can (section 7.3) by weighing the portion removed from the part of the cell corresponding to the region illuminated by the neutron beam. The ratio was found to be 75% gel to 25% solution, so the correction applied was

$$F(Q)_{\text{gel}} = 1.33(F(Q) - 0.25F(Q)_{\text{solution}}) \quad (7.1)$$

This might however be an underestimate of the volume of solution, because of the difficulty of removing all the solution from around the gels. This would lead to errors in the region $1.5\text{\AA}^{-1} < Q < 4\text{\AA}^{-1}$, where features common to both the solution and the sample data (figure 7.7) occur. These are still present in the sample data after correction by equation 7.1. While it is reasonable to expect features in common between the solution and the gel, these might have become enhanced by incomplete subtraction of the solution data.

7.4.3 Fitting of Multiple Scattering and Absorption Corrections

It was found that for all four samples the total structure factors calculated from data collected at $2\theta = 35^\circ$ became negative at values of Q below $\sim 1\text{\AA}^{-1}$. This was due to the calculated multiple scattering correction being too large, because the program used to calculate the corrections assumes that the sample is an infinite flat plate. In reality, at this scattering angle the beam footprint is wider than the sample can and so a significant proportion of the beam is going through the end of the can rather than the side. Because the ends of the can are thicker than the sides, and TiZr is strongly absorbing relative to the sample, this will reduce the observed multiple scattering.

This effect was compensated for by reducing the sample length used in calculating the absorption and multiple scattering while keeping the external length of the cell constant, effectively increasing the cell thickness in the calculation. The variable representing the sample length was progressively reduced until the corrected 35° data coincided with the 5° data in the manner shown in figure 7.5. This is a reasonable procedure because i) it gives consistent results over the whole of the overlap region, and ii) it is found that the adjustment needed is identical for all four samples, the length of the sample being reduced in the calculation from 19mm to 10mm in each case.

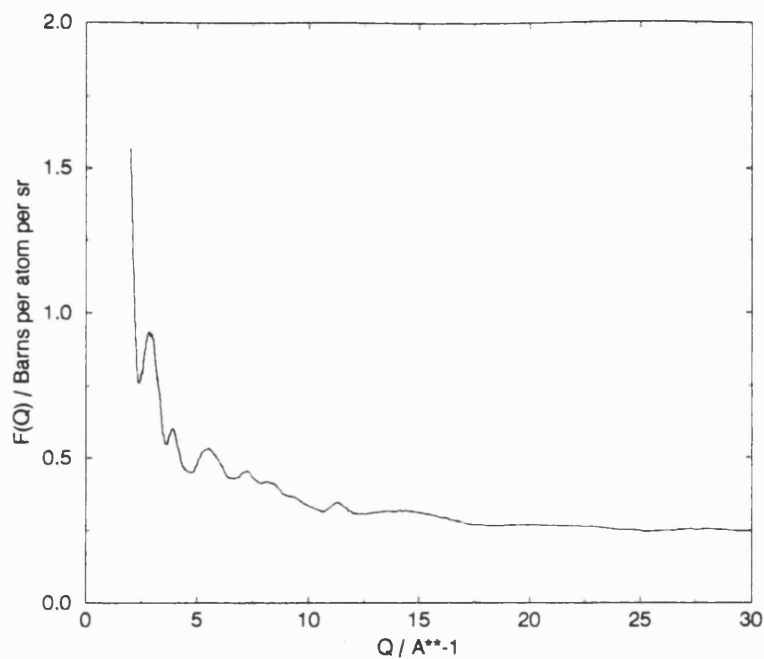


Figure 7.6. The total structure factor for the $\text{C}_3\text{D}_7\text{ND}_3$ vermiculite gel, measured at $2\theta = 150^\circ$.

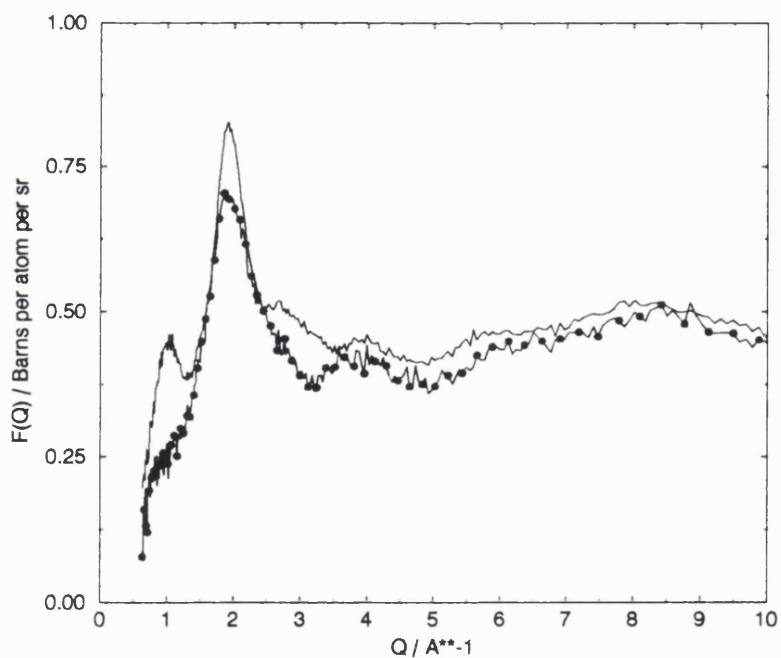


Figure 7.7. The total structure factors for the $\text{C}_3\text{D}_7\text{ND}_3$ vermiculite gel (line only) and the 0.5M $\text{C}_3\text{D}_7\text{ND}_3\text{Cl}$ solution (line with ●), illustrating common features between the data sets.

7.4.4 Fourier Transform of the Data

After the solution data had been subtracted the data sets for both gels were Fourier transformed to a radial distribution function, using equation 4.18. It is known that no correlations can occur at distances less than $1\text{\AA}$, a distance corresponding to the shortest atomic separation in the system. The distribution function was therefore set to zero at $r < 1\text{\AA}$, and the data back transformed to obtain a corrected $F(Q)$.

A correction of this kind should be treated with caution however, as truncation of the errors in this manner can potentially lead to spurious features in the fits. This is because errors introduced by data correction are generally smooth in Q space and so do not produce sharp features in real space. If they are truncated then the resulting shape can give sharp features in real space, even though the ‘total’ error has been reduced.

The fitting procedure (section 7.6) was therefore carried out for data sets with and without this correction and it was verified that no peak positions changed between the two fits. Using the uncorrected data gave a lower R-factor, but reduced the total scattering length density in the fitted unit cell to a less realistic level. The fits presented are therefore those made to the back transformed data sets.

7.5 Data Fitting

The corrected data sets are shown in figure 7.8. The inverse Monte Carlo fitting routine described in section 5.8 was used to fit a common and difference profile to these data sets. There were however several alterations in the procedure. These are outlined below.

7.5.1 Subtraction of The Self Scattering

The intensities shown in figure 7.8 are not Bragg intensities. For the purposes of the Fourier transform described in 7.4.4 the samples were treated as amorphous (equation 4.18) and the self scattering subtracted (section 4.3.3). The data therefore represent the distinct part of the coherent scattering, which oscillates about zero. On the other hand the fitting routine described in chapter 5 calculates the total coherent scattering from a crystallographic definition of the structure factor (equation 4.14). In order to compare the calculated values to the data the program was adjusted by Professor Soper to subtract a self scattering term (equation 4.8). The R-factor, χ^2 , used in the program was then given by (section 5.8)

$$\chi^2 = \sum_{1,f} \left(D(Q)_{meas} - N \left(I(Q)_{calc} - \sum_{\alpha} c_{\alpha} b_{coh,\alpha}^2 \right) \right)^2 \quad (7.2)$$

where the symbols have the same definitions as in section 5.8 and the summation representing the self scattering is taken over all the particles in the fitting arrays. The arrays were set up to contain a number of particles corresponding to the known number of atoms in the system. Although this is an unusual treatment, in that it mixes crystal and amorphous terminology, it is perfectly valid since different definitions of the coherent scattering must be equivalent.

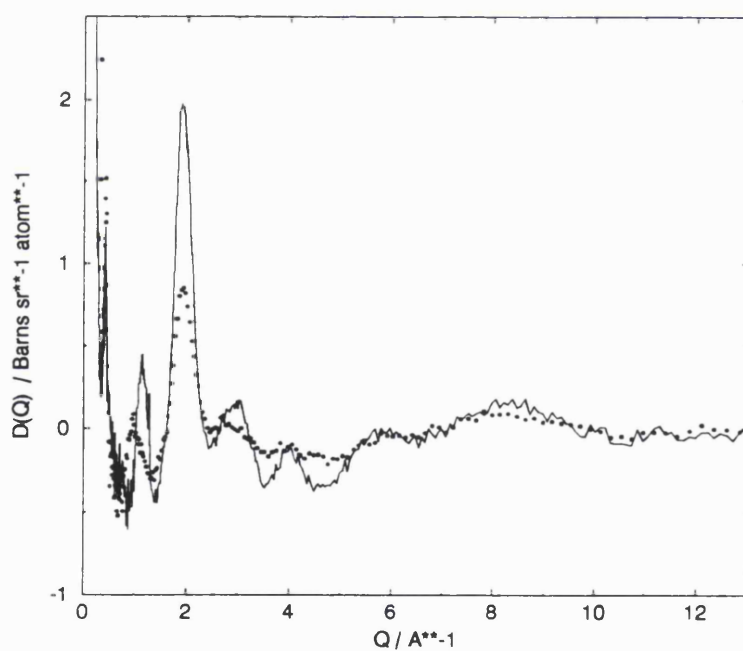
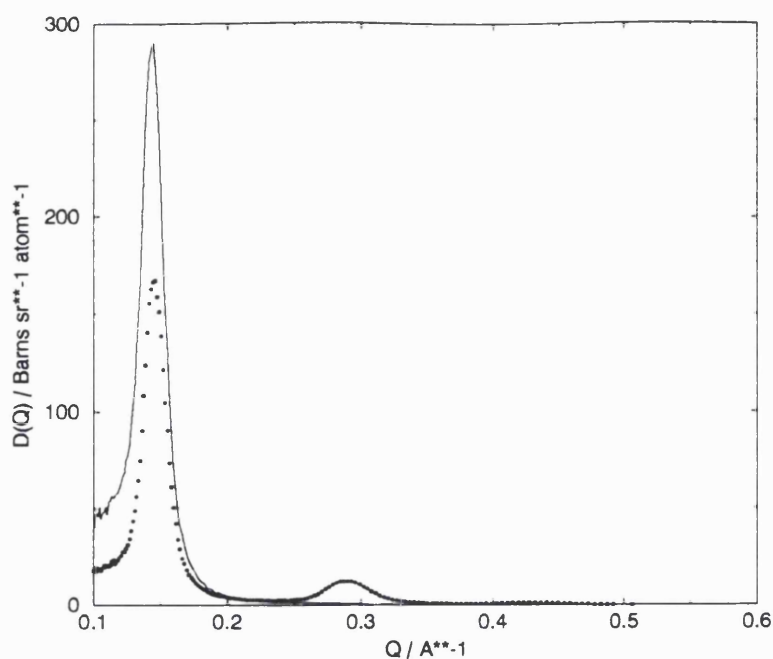


Figure 7.8. Plot of the distinct scattering as a function of Q for the hydrogenated (solid line) and deuterated (filled circles) gels. The top figure illustrates the differences in the (001) and (002) Bragg reflections which result from isotope substitution. The lower figure shows the data at higher Q , illustrating differences in the range $Q = 1 - 6 \text{ \AA}^{-1}$.

7.5.2 Integration of Peak Intensities

As shown in figure 7.8, only the first three ($00l$) peaks are individually resolved. It is therefore not possible to obtain discrete integrated intensities, and the following procedure was used instead. For the (001) to (003) peaks, which are individually resolved, the peaks were integrated and divided by their separation in Q space ($0.144\text{\AA}^{-1}$). To a first approximation this quantity is in the same relation to the peak area as is the level of the distinct scattering from an unresolved peak, so, for the (004) and higher order peaks, the fit was made directly to the level of distinct scattering at appropriate values of Q . This procedure therefore gave the relative intensities for each 'Bragg peak'. The intensities obtained covered a Q range of $0.07 - 12\text{\AA}^{-1}$, this being equivalent to the first 83 ($00l$) peaks.

7.5.3 Averaging the Density Profiles

Because the gels are expected to contain some ordering which is only short range it was necessary to average it out in the fitted density profiles (section 4.3.5). The fitting arrays were therefore expanded to simulate five unit cells, and the fitted density profiles averaged over all five of these. The profiles were also averaged as previously over the last 10^4 steps of the fitting procedure.

7.5.4 Discrepancy in the Layer Spacing

Although it was not apparent in the uncorrected data, inspection of the (001) Bragg peaks in the corrected data sets showed a slight change in the clay layer spacing, from $43.6\text{\AA}$ in the hydrogenated sample to $43.3\text{\AA}$ in the deuterated sample. This could

be an isotope effect, but it is by no means conclusive as changes in the clay layer spacing could occur as a result of very small changes in the soaking solution.

The difference was assumed to have no effect on the electrical double layer structure and a spacing of 43.6Å was used for both samples. This is reasonable if it is assumed that a liquid-like region separates any double layer structures associated with the clay surfaces. This is expected on the basis of previous results (Woessner 1979, Xia et al 1995 for example).

7.6 Results

Table 7.1 lists the optimised fitting parameters, with the intensities I_a and I_b being the average intensity in each of the five unit cells simulated by the fitting routine. Complete fits to both data sets are shown in figure 7.9. The common and difference density profiles, averaged over the five cells, are shown in figure 7.10, with the integrated peak intensities in table 7.2.

Parameter	Value
I_a	67.7
bg_a	0.32
I_b	4.64
bg_b	0.0
χ^2_1, χ^2_2	1.00, 1.01
N_1, N_2	0.27, 0.38
σ	1.50

Table 7.1. Table of optimised fitting parameters. Symbols have the same meaning as those in table 5.3.

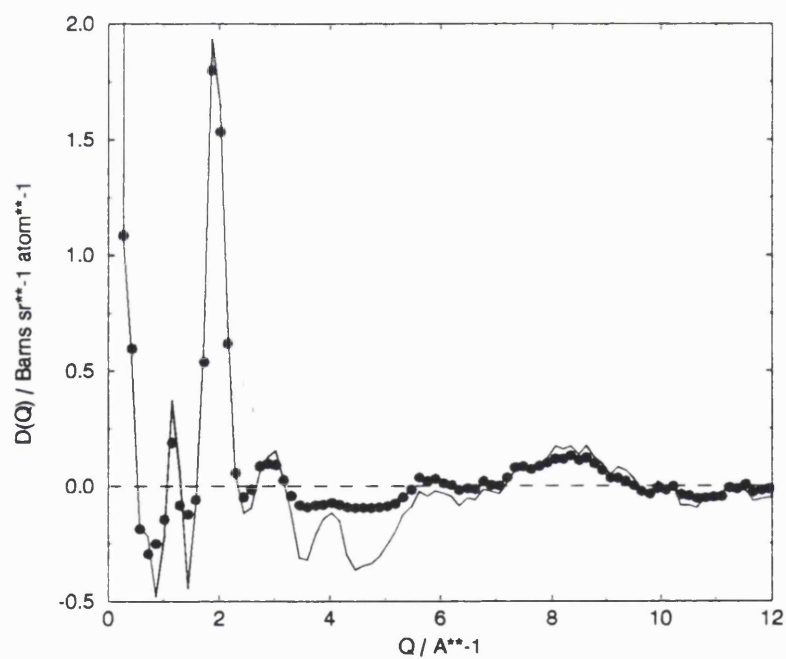
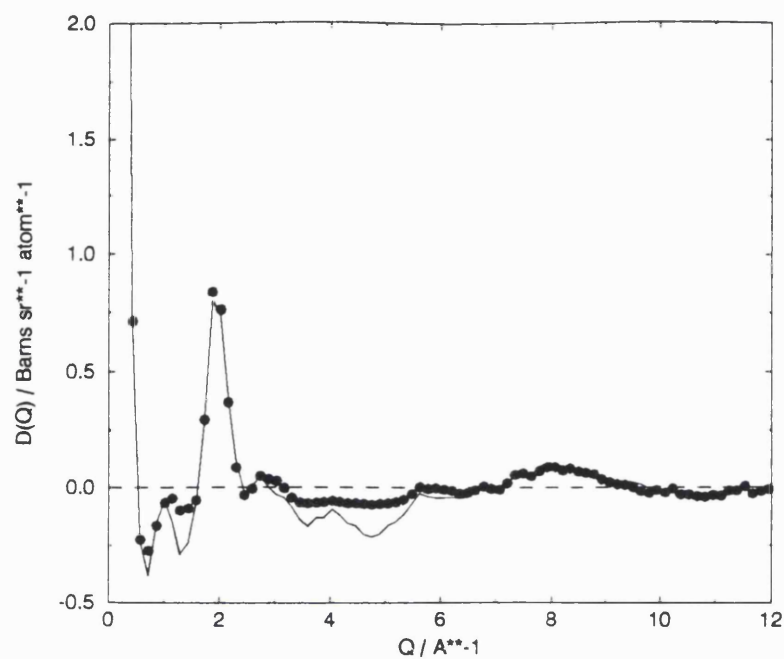


Figure 7.9. Comparison of the measured (line) and calculated (filled circles) distinct scattering from the deuterated (upper figure) and hydrogenated (lower figure) gels. Fits to the (001) to (003) peaks are not shown because of scale limitations but were excellent ($<<1\%$) for both data sets.

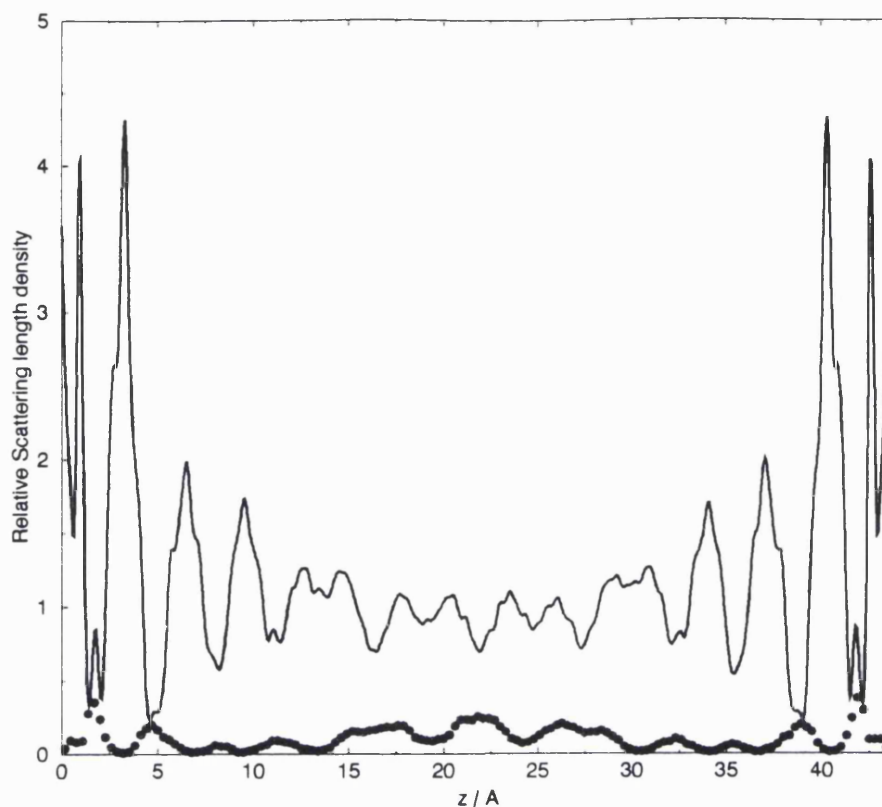


Figure 7.10. Fitted common (line) and difference (filled circles) components of the scattering length density profile in $C_3D_7ND_3$ and $C_3H_7ND_3$ vermiculite gels in D_2O as a function of position on the clay c^* axis and averaged over five unit cells. The origin is set at the centre of the clay layer.

Position	Assignment	Profile	Area	Chemical Equivalent
0.0 - 0.64	O_h Cations	Common	1.58	O_h cations, (0.79)
0.64 - 1.46	O (clay)	Common	1.75	3 O
1.46 - 2.1	D (clay)	Common	0.384	0.6 D
2.1 - 4.8	T_h cations, O (clay), H_2O	Common	5.24	T_h cations, 3O, 1.4 D_2O
0.9 - 3.3	H / D (clay)	Difference	0.35	0.6 H / D
4.8 - 8.1	D_2O	Common	3.7	1.93 D_2O
3.3 - 6.7	H / D (D_2O)	Difference	0.33	0.6 H / D
8.1 - 11.1	D_2O	Common	3.5	1.81 D_2O
11.1 - 32.5	D_2O , C_3 - ND_3	Common	21.2	0.65 C_3 - ND_3 , 9.5 D_2O
13.4 - 30.2	H / D (alkyl)	Difference	1.06	0.61 H_7

Table 7.2. Analysis of peak areas in the fitted neutron scattering density profiles in figure 7.10 showing: the limits of integration (Å); the assignment of chemical species to each peak; which profile the peak occurs in; the peak area ($10^{-14}m$); the number of atoms corresponding to these areas. The areas and number of species are given per unit cell.

7.7 Discussion of Errors and Uncertainties in The Fits

Figure 7.11 shows that the fitted density profiles with error bars.

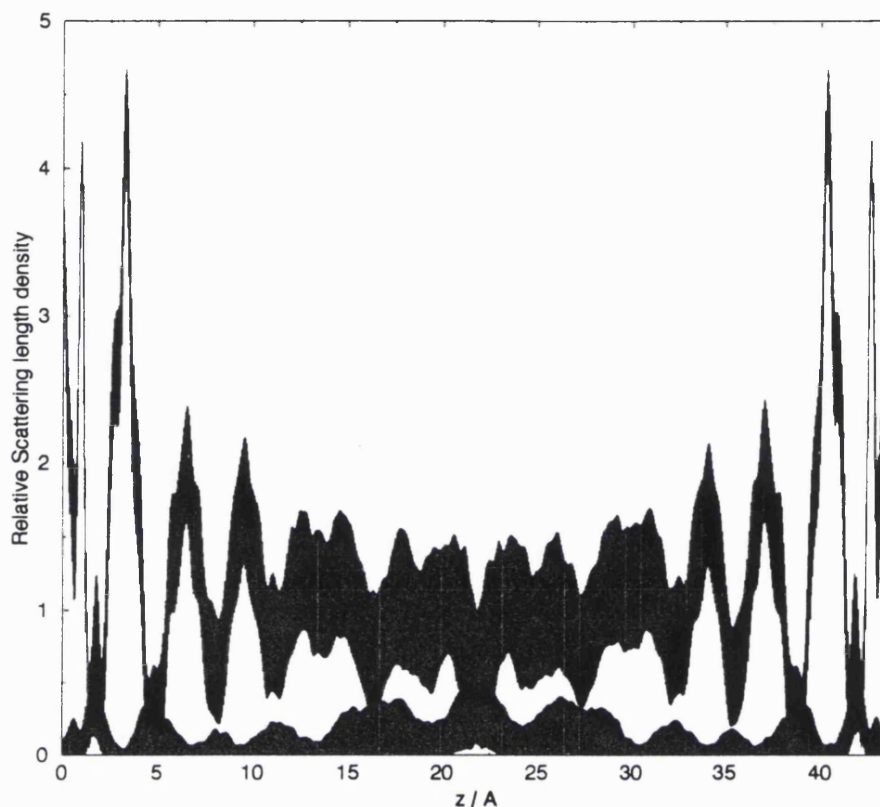


Figure 7.11. Fitted density profiles as in figure 7.10, plotted with error bars.

It can be seen from figure 7.11 that the errors are large compared to the size of features in the centre of the interlayer region ($\sim 13-30\text{\AA}$), but are smaller relative to features in and near to the clay layer region. This is due to the greater degree of long range order which is found near the clay layers. In the centre of the interlayer the ordering is principally liquid-like, and consequently there are differences in the five individual profiles which are being averaged to produce the profile. The larger error bars in this region reflect these differences.

A principal advantage of these experiments over those on the crystalline vermiculites is that the isotope substitution was carried out *in situ*, thus minimising errors arising from irregularities in the samples. It is possible however that the sample was disturbed by the needle used to replace the solution. Also if the gels were not perfectly aligned within the can it is possible that the orientation of the can was slightly different between runs, as there were no external features of the can to identify a 180° rotation. However, for all four samples the data in the overlap region between the differential cross sections obtained at 5° and 35° were consistent, suggesting that these errors were smaller than the level of statistical error. It is however likely that the data contain errors arising from subtraction of the solution data, as described in 7.4.2. Figure 7.9 shows that the fit to both data sets is worst for $Q \sim 3\text{--}5.5\text{\AA}^{-1}$, where the fitting only weakly reproduces two dips occurring at $Q \sim 3.5$ and $Q \sim 4.5\text{\AA}^{-1}$. This a region where there are significant features in the solution data (figure 7.7) and it is therefore possible that these oscillations have become exaggerated by this stage in the correction procedure.

Apart from this the fits reproduce both data sets over the whole Q range, with the exception of some quantitative deviation in both fits around $Q = 1\text{\AA}^{-1}$. Both fits do however reproduce this peak qualitatively.

Finally the same consideration of uncertainty in the gel composition (and so in the accurate determination of the background level) as described in section 5.11 applies to the areas assigned in table 7.2.

7.8 Structural Assignment

The density profiles represent the average for a system containing a considerable degree of liquid-like ordering. While oscillations in the profiles indicate structuring of the interlayer, a large part of the intensity is present as a structureless block beneath these oscillations (figure 7.10 and 7.11), indicating that all parts of the interlayer contain some degree of disorder. It is important to remember this when visualising the structural assignment which follows.

7.8.1 The Counterion Distribution

The location of the counterion alkyl groups is clearly identified by a broad peak in the difference profile in the region 13 to 30Å whose area corresponds to 4.2 deuterium atoms. This is the equivalent of 0.6 D₇ groups, which is consistent with there being 0.65 cations per unit cell of which ~90% are deuterated. It is therefore clear that the counterions are not located next to the clay surfaces but instead are broadly spread across the interlayer region. It should also be noted that the volume of this region is 3-4 times that of the counterions. This shows that segregation of water and counterions does not occur. The assignment is also supported by a broad dip observed in the average level of the common profile across the same region. This is expected to occur because the sum of the scattering lengths per unit volume is lower for the unsubstituted part of the ions than for D₂O.

The maximum counterion density is located in the mid-plane of the interlayer. This indicates that not only are the counterions not bound to the surface but furthermore that they are not separated into two groups associated with each of the surfaces, as would be expected if they followed a Poisson-Boltzmann distribution. The difference

profile does indicate the position of the alkyl groups rather than the charged ND_3^+ groups, but as the separation of the nitrogen from the furthest alkyl protons of the ion is less than $5\text{\AA}$ there must be a significant number of ND_3^+ groups located more than $10\text{\AA}$ from the charged clay surfaces.

The peak in the difference profile does in fact have some structure, being divided into three maxima covering $\sim 5\text{\AA}$ each, each of these being associated with a minimum in the common profile (figure 7.10). It is possible that the ions are sitting in three layers with water molecules forming layers between them, a situation which would be consistent with the width of the peaks in the difference profile. This is very speculative however, especially in view of the large errors associated with this part of the profile (figure 7.11).

The conclusion that the ions are located mainly around the centre of the interlayer is also consistent with a direct inspection of the data. It is observed that deuteration of the counterions enhances the (002) Bragg peak relative to the (001) (figure 7.8). Since the scattering length of hydrogen is negative and that of deuterium is positive (table 4.1) this indicates that a majority of the substituted species must be located in a portion of the unit cell where the cosine function in the Fourier Transform (equation 4.15, figure 4.4) is negative for the (001) reflection and positive for the (002). The only region satisfying both these conditions is the central quarter of the unit cell, i.e. the centre of the interlayer.

7.8.2 The Water Structure

Having located the counterions it is concluded that the strong peaks in the common profile (figure 7.10) at 6.6 and $9.6\text{\AA}$ (and their equivalents at 37.0 and $34.0\text{\AA}$)

must be due to water, indicating the presence of at least two layers of water molecules at each of the clay surfaces. This is consistent with the peak separation of 3Å. It should be noted that only around half of the total scattering intensity in these regions is resolved into individual peaks, suggesting that even near the surface there is a significant degree of disorder.

The common profile also contains scattering from the Cl⁻ ions present in the form of excess salt inside the gel. On the basis of a salt fractionation ratio of 3 (section 6.3.4) it is expected that there will be 0.05 ion pairs per unit cell. The position of the Cl⁻ ions cannot be identified in this experiment and it is possible that they might contribute to these peaks. The total scattering length due to Cl⁻ will only be 0.07×10^{-14} m per unit cell however (compared to 1.9×10^{-14} m for a single D₂O molecule), so the peaks seen must be principally due to water molecules.

The areas under the peaks are equivalent to 1.9 and 1.8 water molecules in the first and second layers respectively, compared to the 2.2 molecules which would be expected assuming the water density to be 1 g cm⁻³. Within the uncertainty introduced by i) the background level, and ii) the possibility of incomplete deuteration of water inside the gel, there is therefore no conclusive evidence for this structured region being significantly different in density to bulk water. It is also not possible to identify conclusively the orientation of water molecules in this region, although it seems reasonable to assume that they will be mainly orientated with the oxygen away from the negatively charged surface (Toney et al 1995).

The remainder of the common profile shows some structuring, although the errors associated with the profile are much larger than the peaks in this region (figure 7.11). There are four broad peaks in the region $z = 11.1$ - 32.5 Å, each of which is divided into two subsidiary peaks. The first occurs at 12.6 Å, 3 Å from the second water peak.

This might indicate a third water layer, or might be due to the ND_3^+ groups of the counterions. In either case this ordering is very weak, the peak representing only a small part of the total fitted intensity.

Finally, it is observed that the difference profile shows distinct peaks at around $1.7 / 41.9\text{\AA}$ and $4.7 / 38.9\text{\AA}$. It is likely that these are due to ongoing exchange of H / D in the clay hydroxyl groups and in water absorbed on the clay surface. While there is no information available on this system, studies of mica at elevated temperatures (Vennemann and O'Neil 1996) indicate that this exchange can take place over the timescale of this experiment (which was 6 days from the sample being put into D_2O until the measurements on the first sample were made, and another 4 days before measurements on the second). Furthermore there is a peak observed at $1.7\text{\AA}$ in the common profile which indicates partial exchange of the hydroxyls in the first sample, and the total area of these two peaks represent 1.2 H / D atoms. Within the errors introduced by the background this is consistent with the expected one hydroxyl group per unit cell.

7.9 Conclusion

The results presented in this chapter can be summarised in two main points. Firstly, the charge sites on the clay surfaces interact more favourably with water molecules than with the counterions. The ordered region near the surface is found to consist of two layers of water molecules, rather than the a layer of counterions as is postulated in the Stern Layer. The water molecules are presumably orientationally ordered, although this cannot be determined from this experiment. There is no (conclusive) evidence for ordering of water molecules beyond these two layers.

Secondly, the counterion density is at its maximum in the centre of the interlayer, indicating that even outside the region of water structuring they do not follow the Poisson-Boltzmann distribution predicted by primitive models. This distribution might however develop if the clay layer spacing was increased.

These results are important in showing the extent to which primitive models can be applied to systems of this sort. Their significance is discussed in chapter 8.

Discussion

8.1 Contents

This chapter summarises and discusses the results presented in the thesis, in terms of both their relation to previous results and their significance in understanding the systems studied. Profitable areas for future study are also identified.

8.2 Swelling versus Non-Swelling Vermiculites

8.2.1 Summary of Results

Alkyl-ammonium vermiculites exhibit macroscopic swelling behaviour only when the alkyl chain of the counterion is 3 or 4 carbon atoms in length. Experiments were carried out (chapter 5) to compare the interlayer structures in hydrated crystalline BuNH₃ and MeNH₃ vermiculites, with the aim of clarifying the reasons for this transition from non-swelling to swelling to non-swelling behaviour as the alkyl chain length is increased. The experiments showed that:

- i) MeNH₃ ions lie with an angle between the C-N bond and the plane of the clay layers in the range 0-50°, while BuNH₃ ions lie principally with the C-N bond perpendicular to the clay layers.
- ii) In both systems the counterions are only weakly bound to the clay surfaces.

iii) In MeNH₃ vermiculite a distinct layer of water molecules is associated with each clay surface. This was not clearly observed in BuNH₃ vermiculite.

8.2.2 Orientation of The Counterions

The interlayer structures observed in the two systems are similar in several respects. In both cases the interlayer is rather weakly ordered and the counterions are hydrated. The results do however show that increasing the alkyl chain length causes a reorientation of the counterions, as the counterions become too large to lie parallel to the clay surfaces. This is consistent with the observed layer spacings in short chain ($n_c < 7$) alkyl-ammonium Eucatex vermiculite. These were determined using X-ray diffraction to locate the first 12 (00 l) Bragg reflections and are listed in table 8.1.

Counterion	n_c	Layer Spacing / Å	$\Delta H_{\text{solvn, D2O}} / \text{kJ mol}^{-1}$
MeNH ₃ ⁺	1	12.3	5.86
EtNH ₃ ⁺	2	12.7	8.49
PrNH ₃ ⁺	3	18.6	0.92
BuNH ₃ ⁺	4	19.4	-3.35
PtNH ₃ ⁺	5	20.6	-1.80
HxNH ₃ ⁺	6	21.8	0.17

Table 8.1 Comparison of short chain alkyl-ammonium ions, showing the number of carbons in the alkyl group (n_c) and the observed layer spacing of Eucatex vermiculite containing these counterions, measured at 26°C and 100% relative humidity. The enthalpies of solvation in D₂O of the bromide salts of the ions at 25°C are also shown.

A very marked increase in the clay layer spacing is observed between EtNH₃ and PrNH₃ vermiculite. This is consistent with a change in orientation of the ions occurring between the non-swelling and swelling alkyl-ammonium clays. Comparison of the series BuNH₃ to HxNH₃ shows a regular increase of 1.2Å for each added CH₂ group. This suggests that the longer alkyl chains assemble into a regular structure, consistent with the model described in section 3.3.2 in which the alkyl chains form an angle of 54° with the clay surfaces.

8.2.3 Thermodynamics of Counterion Hydration

Table 8.1 shows the enthalpies of solution of the bromide salts of the alkyl-ammonium ions (Krishnan and Friedman 1970). It is seen that these are all relatively small (<10kJmol⁻¹). The hydration of PrNH₃Br is endothermic, but it is exothermic for BuNH₃Cl. There is no systematic trend in either the sign or magnitude of ΔH down the series.

Measurements have been made of the changes in enthalpy and entropy associated with hydration of the tertiary ammonium salts R₄NX, where R=Me to Bu and X=Br, I (Sarma et al 1969). The change in enthalpy varies unpredictably in a manner similar to the primary amine salts, values being found between +42 and -8.6kJmol⁻¹. The entropy change increases rapidly as the alkyl chain length is increased, the results for the series Me₄NBr to Bu₄NBr being 42.2, -138, -471 and -749JK⁻¹mol⁻¹ respectively. This trend is consistent with the current picture of greater ordering being imposed on water molecules by hydrophobic hydration (section 2.3.2). This is probably the principal factor which prevents long chain alkyl-ammonium vermiculites from swelling, and explains the micelle-like structures which these counterions form in the interlayer. It does not

however explain why macroscopic swelling behaviour is not seen in MeNH₃ and EtNH₃ vermiculites.

8.2.4 Proposed Mechanism for Macroscopic Swelling

There is no clear reason for the lack of swelling behaviour in MeNH₃ and EtNH₃ vermiculites, from considerations of either i) the state of hydration of the counterions in the interlayer, or ii) the thermodynamics of the counterion hydration.

It is therefore proposed that macroscopic swelling behaviour occurs in PrNH₃ vermiculite because the clay layers are forced apart by the increased size of the counterions and the consequent re-orientation relative to the clay layers. This weakens the Coulombic interactions which oppose macroscopic swelling. The swollen phase therefore becomes (under certain conditions) the thermodynamically favoured phase.

The interlayer structures in longer chain ($n_c > 4$) alkyl-ammonium vermiculites were not investigated in these experiments due to the limit of available neutron beam time. The structure assigned for BuNH₃ vermiculite is however comparable to that observed in HxNH₃ and OctNH₃ (C₈H₁₇NH₃) vermiculites (Johns and Sen Gupta 1967). It is therefore proposed that the absence of macroscopic swelling is caused by the increasing entropic cost of hydration of the counterions.

8.3 The Electrical Double Layer Structure

8.3.1 Summary of Results

Measurement of the interlayer structure in a macroscopically swollen PrNH_3 vermiculite gel (chapter 7) showed that

- i) The counterions are located in a broad distribution centred on a maximum at the mid-plane of the interlayer region: none are adjacent to the charged clay surface. The counterions are not segregated from the water molecules.
- ii) There are two well defined layers of water molecules associated with each of the clay surfaces, the separation of these layers being $3.0\text{\AA}$. It was not possible to distinguish any preferential orientation of water molecules relative to the clay surface. No conclusive evidence of restructuring of the water molecules beyond these two layers was seen, although it is possible that a very weakly ordered third layer is present.

8.3.2 Comparison with Previous Results

Previous experiments have indirectly measured the ion distribution in vermiculite gels with larger clay layer spacings ($>100\text{\AA}$). Calculations of the surface charge from the swelling pressure (assuming that this arises from a purely electrostatic repulsion) have shown that $\sim 90\%$ of the counterions are absorbed onto the clay surface (Crawford et al 1991).

More recently Swenson et al (1997) have proposed that the counterions in a BuNH_3 gel with a layer spacing of $\sim 100\text{\AA}$ are located in a $3\text{\AA}$ thick layer between $11\text{\AA}$

and 14Å from the centre of the clay layer. This is based on a qualitative interpretation of the pair distribution functions for two gels containing the counterions $\text{C}_4\text{H}_9\text{ND}_3^+$ and $\text{C}_4\text{D}_9\text{ND}_3^+$. However, the two gels studied had different layer spacings (90Å and 130Å) and the method assumed that this discrepancy does not affect the pair distribution functions for $|\mathbf{r}| < 30\text{Å}$.

This result is in agreement with the results presented here in showing that the $\sim 6\text{Å}$ region adjacent to the clay surface consists of water molecules. The two layers of water seen in the results presented here are also qualitatively consistent with the results of Soper and Gromek for a Na montmorillonite, although the latter were not published because of a lack of data at low Q .

The observed water restructuring is also consistent with measurements made on a variety of other surfaces, as described in sections 2.5 and 2.6. The principal points of comparison are summarised below.

Surface force measurements between mica surfaces (Israelachvili 1983) showed four pronounced oscillations in the surface-surface force as they are brought into contact, these oscillations having a periodicity of $2.5 \pm 0.3\text{Å}$. The results in this thesis are consistent with interpreting these as arising from disruption of surface water layers, although the periodicity is somewhat less than the 3.0Å which would be expected from the propyl-ammonium vermiculite results. Surface force measurements on PrNH_3 vermiculite would provide an interesting comparison.

The reflectivity measurements of Toney et al (1995) showed the presence of three layers of water molecules on a negatively charged Ag surface, as well as evidence of reorientation of the water molecules induced by the charged surface. They found a distance of 3.7Å between the surface Ag atoms and the first maximum in the oxygen density: this is 0.4Å greater than the 3.3Å from surface oxygen to first maximum found

in the vermiculite. These results are comparable, considering that i) the van der Waals radius of Ag is 1.7Å vs 1.5Å for O, and ii) the neutron scattering lengths of oxygen and deuterium are roughly equal, unlike their X-ray scattering lengths. If the hydrogen atoms of the water molecule are orientated towards the surface (and cannot be individually resolved) then, in a neutron diffraction experiment, the first maximum will appear closer to the surface than the plane of the oxygen atoms. This comparison therefore suggests that the same orientation occurs in both systems, namely that both hydrogen atoms on the water molecule are pointing towards the surface.

The presence of water molecules at the surface in preference to the counterions is also consistent with computer simulations of a variety of systems (section 2.5; Rose and Benjamin 1991, Philpott et al 1995 for example).

8.3.3 Discussion

The results presented here are perhaps surprising in that the counterions are located a long way from the charge sites on the clay surface. The results are also in opposition to traditional models of the electrical double layer. As has been shown in section 8.3.2 however the presence of two restructured layers of water molecules at the clay surface is consistent with a wide variety of experimental and computer simulation results. It should also be remembered that primitive models of the EDL neglect water structure and so are unable to reproduce features such as this. Furthermore, considering the clay layers as flat macro-ions, this is precisely the kind of water structure which is expected by analogy with the hydration shells formed around ordinary ions in solution (section 2.3.1).

Two questions arise however as to how representative the measured ion distribution is of colloidal systems in general. Using PrNH₃ vermiculite allows preparation of a clay layer spacing of ~40Å and isotopic labelling of the counterions, but introduces an extra factor in the non-polar alkyl groups on the counterions. It might be argued that the ion distribution is then determined by hydrophobic hydration of the counterions and that this result cannot be compared with clays which contain simple metal counterions. This view is supported by the negative entropy observed for the crystal to gel transition in BuNH₃ vermiculite (Smalley et al 1989) which could be attributed to hydrophobic hydration of the counterions.

At any given concentration, the gel to crystal transition temperature is higher for PrNH₃ than for BuNH₃ vermiculite and the transition is not observed at all in Li vermiculite. At the transition temperature the gel and crystal phases are in equilibrium and so

$$\Delta H_{sw,T_c} = T_c \Delta S_{sw,T_c} \quad (8.1)$$

where $\Delta H_{sw,T_c}$ and $\Delta S_{sw,T_c}$ are the enthalpy and entropy changes associated with swelling at the phase transition temperature. The thermodynamics of the swelling transition have not been measured for PrNH₃ vermiculite and so it is not possible to say for certain whether this increase in T_c is due to a decrease in the entropy loss or an increase in the enthalpy gain on swelling. A decrease in the entropy loss as the size of the non-polar groups is decreased is however consistent with the accepted model of hydrophobic hydration of the counterions.

If the enthalpy change on swelling were the same for both systems, and assuming the entropic cost of swelling to be proportional to the surface area of the hydrophobic group (section 2.3.2), then the values of T_c found in BuNH₃ vermiculite would be expected to be ~0.75 times those for PrNH₃ vermiculite. For BuNH₃ vermiculite in

0.1M solution T_c is 282K (figure 3.7b), while for PrNH_3 vermiculite in the same conditions T_c was found to be 332K (table 6.2). This gives a ratio of 0.84. These relative magnitudes support hydration of the alkyl groups as a significant factor in determining the swelling behaviour of the alkyl-ammonium vermiculites.

There is however no evidence to suggest that aggregation of the counterions occurs below the phase transition temperature. The difference in partial molar volumes at infinite dilution of PrNH_3Br and NH_4Br in H_2O is $51\text{cm}^3\text{mol}^{-1}$ (Desnoyers and Arel 1967). Taking this difference to equal the volume of the propyl groups means that they occupy $86\text{\AA}^3$ per alkyl group. In one unit cell of a $43.6\text{\AA}$ PrNH_3 gel, assuming that there are 0.75 counterions, the alkyl groups will occupy $\sim 64\text{\AA}^3$. The volume across which the alkyl groups are observed to be present in the density profiles for the gel is $408\text{\AA}^3$ per unit cell, thus showing that the water molecules and counterions are not segregated.

Furthermore, micelle formation is not expected from the behaviour of PrNH_3^+ in bulk solutions. The critical micelle concentration (CMC) for a surfactant with a single straight alkyl chain is given by

$$\log[\text{cmc}] = b_0 - b_1 n_c \quad (8.2)$$

where n_c is the number of carbons in the chain and b_0 and b_1 are constants characteristic of the class of surfactant (Hunter 1993). For alkyl-ammonium chlorides these values are 1.25 and 0.265 respectively, so for PrNH_3Cl (aq) the CMC is 2.85M. This compares with an effective concentration of counterions inside a $43.6\text{\AA}$ gel of $\sim 2\text{M}$. The separation of the counterions from the charged clay surfaces therefore appears to be principally determined by the favourable interaction of water molecules with the surface rather than by aggregation of the alkyl groups.

A second factor which must be considered with the counterion distribution is that in the vermiculite gels the separation of the clay surfaces was only 37.0Å. This represents the very smallest end of the length scales typical of colloidal systems, which can exhibit equilibrium separations up to the order of micrometers (Matsuoka et al 1996, Ito et al 1994). It may be the case that a greater surface separation is needed to allow the full double layer structure to develop.

The question is then, how would the ion distribution in the clay gel develop if the layer spacing were to be increased? Does the observed distribution indicate that the ions will always sit midway between the clay surfaces, or is it in fact the product of two diffuse distributions which happen to overlap because of the small surface-surface separation? Considering that restructuring of the water is limited to the immediate vicinity of the clay layers the latter appears more likely. It would however be extremely interesting to measure the ion distribution in gels with larger layer spacings, possibly using uniaxial stress to allow a continuous variation of the layer spacing. The application of uniaxial stress would also allow comparison of gels with the same layer spacing but with different counterions.

The current method is limited however by the shift with increasing layer spacing of the (001) Bragg peak to lower Q , requiring an even greater Q range to observe this peak while maintaining good real space resolution. Future experiments could perhaps be carried out on the planned GEM diffractometer at ISIS, which is intended to have a detector bank at $2\theta = 2^\circ$ (Eccleston (ed) 1997). This would allow studies with layer spacings up to $\sim 125\text{\AA}$, three times that used in the experiments described here. Instruments such as D16 at the ILL (Grenoble) would also allow gels with layer spacings of $>100\text{\AA}$ to be investigated, although with a much lower real space resolution of $\sim 3\text{\AA}$. In conjunction with deuteration of the counterions this would still be sufficient

to distinguish between different possibilities for the counterion distribution, although it would not be possible to resolve the water structure.

Conclusion

The interlayer structure and swelling behaviour of alkyl-ammonium Eucatex vermiculites have been investigated by neutron diffraction. It was found that macroscopically swollen PrNH_3 vermiculite gels behave as typical one dimensional colloids, exhibiting a clay layer spacing proportional to $c^{-1/2}$ as predicted by theories based on the primitive model (Hunter 1993). Measurement of the interlayer structure in crystalline MeNH_3 and BuNH_3 vermiculites showed that macroscopic swelling is not caused by surfactant behaviour of the counterions. Furthermore there is no indication that the interlayer structure in swollen PrNH_3 is determined by aggregation of the counterions. The structure observed in the swollen PrNH_3 vermiculite gel is therefore argued, within the context of the small clay layer spacing used, to be representative of a typical colloidal system.

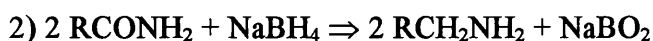
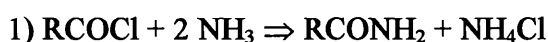
The measurement of the interlayer structure in a PrNH_3 vermiculite gel, which represents the first direct measurement of an electrical double layer structure in a colloidal system, shows that the water structure near the charged clay surfaces is highly perturbed from that of bulk water. Two distinct layers of water molecules are seen adjacent to the surface, although there is little evidence of restructuring beyond this. Although this result is contrary to generally accepted models it is consistent with previous results from computer simulations (Rose and Benjamin 1991), X-ray reflectivity (Toney et al 1995) and surface force measurements (Israelachvili 1983). The results therefore show that although primitive models can reproduce colloidal behaviour at greater separations they are unrealistic in the region adjacent to the surface.

Furthermore, the maximum counterion density occurs at a point midway between the clay layers, in direct opposition to the Poisson Boltzmann distribution of the generally accepted primitive models. Further experiments are needed to establish whether this represents the full electrical double layer structure or if a Poisson Boltzmann distribution would be observed with a larger surface separation.

Appendix A

Synthesis of ^{15}N Butyl-ammonium Chloride

The amine hydrochloride $\text{C}_4\text{H}_9^{15}\text{NH}_3\text{Cl}$ was synthesised by a two stage procedure involving reaction of the acid chloride $\text{C}_3\text{H}_7\text{COCl}$ with $^{15}\text{NH}_3$ (aq) to give the amide $\text{C}_3\text{H}_7\text{CO}^{15}\text{NH}_2$ (Vogel 1980) followed by reduction of the amide to the amine with NaBH_4 (Wann et al 1981).



This procedure was selected as being most suitable for the facilities available, and proved successful although giving an extremely low yield of the product.

Procedure: Step 1

15ml of a 3.3M aqueous solution of $^{15}\text{NH}_3$ (50 mmol) were placed in a 50ml beaker surrounded by crushed ice, and stirred with a magnetic stirrer bar. A 50ml dropping funnel was used to add 2.65g (25mmol) of butanoyl chloride dropwise, while ensuring that no white fumes were lost from the reaction mixture. White crystals of the amide separated out immediately. After addition was complete the reaction mixture was allowed to stand in the ice water for 15 minutes, and the amide crystals were filtered off using a suction filtration pump. The product was then spread on filter papers to air dry. The yield was 1.57g (72%).

Procedure: Step 2

16 mmol (1.39g) of the amide were placed in a 100ml round bottomed flask with 1.61g (40 mmol) of NaBH_4 and 20ml of DMSO (Me_2SO). A mixture of 20ml DMSO and 3.4ml (55 mmol) of MSA (MeSO_2OH) was then added dropwise to the flask over a period of 30 minutes, the reaction mixture being stirred continuously with a magnetic stirrer bar. After this period 100ml of demineralised water was added to redissolve the white gelatinous complex which forms in the reaction mixture, this stage being an addition to the original recipe. The reaction was then quenched by the addition of 20ml of a 10% NaOH (aq) solution.

The product was extracted from the reaction mixture using three 10ml portions of CH_2Cl_2 . These were combined and washed with three 10ml portions of NaOH to remove the remaining DMSO. The product was then extracted using three 10ml portions of HCl (aq), which were combined and dried in a vacuum oven at 60°C and ~ 0.1 atmospheres to obtain the amine hydrochloride. The product was verified by IR spectroscopy, identifying the presence of the N-H stretching band, and also by the distinctive smell of the amine hydrochloride. 0.05g of the product was obtained, representing a yield of 2%.

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