An Investigation into the Structuring of an Hydrophobic Clay in Silicone Fluid

by

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Big whorls have little whorls
Which feed on their velocity,
And little whorls have lesser whorls
And so on to viscosity.

— Lewis F Richardson

DEDICATION

This thesis is dedicated to my mother
And to the memory of my father, Dr A K Lewkowicz

ABSTRACT

Hydrophobic clays are one established route by which non-aqueous fluids may be structured to give viscous fluids (gels). Although known for many years for their role as rheological modifiers, the underlying mechanisms for structuring hydrophobic clay gels are poorly understood. It is the aim of the research described in this thesis to probe the microstructure of these systems and elucidate the major factors contributing to this structuring.

Using a variety of analytical tools, including microscopy, thermal and rheology, the structure of the clay (dimethyl dialkyl quaternary ammonium hectorite) has been followed from its initial dry state through dispersion and final gelation. With silicone fluid as the non-aqueous liquid of interest and utilising a range of polar additives, the role of the additive has been investigated. Similarly, using these same systems, the influence of processing has been investigated over a wide range of shear regimes.

The main findings of this work are a new structural description of the deagglomerated clay, a proposed mechanism for the gel formation and a detailed understanding of the relative contributions of chemical, thermal and mechanical energy on the structure formation. For the first time in this area, a comprehensive study of the effect of process conditions on the dispersion of hydrophobic clay has been completed and is reported here.

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Clays are composed of extremely fine particles of minerals that are layer type aluminium or magnesium silicates. Clay properties are often controlled by the surface properties of the minerals rather than the bulk chemical composition. An overview of the relevant chemistry is given and starts with a brief description of the mineralogy consideration and proceeds to describe the general principles of clay chemistry. It then proceeds to describe the effects of surface coatings, their interactions and applications.

Clays may be categorised into two groups: the hydrophilic clays and hydrophobic clays. Hydrophilic clays, as the name suggests, are clays that display an affinity for water. The chemistry of hydrophilic systems has been extensively studied and reported in the open literature. There is a good understanding of the surface chemistry of hydrophilic clays that has enabled the mechanism of how these clays contribute to structuring fluids to be identified. Hydrophobic clays are species that have been treated with an organic material that results in them repelling aqueous environments. They are also known as organophilic or organically modified clays.

Clays are used in a wide field of applications e.g. ceramics, paper, plastics and rubbers, drilling fluids and paints to name a few. They are incorporated in formulations to aid gelling, thickening and suspension in both aqueous and non-aqueous systems.

The clay of particular interest to this project is a smectite (montmorillonite) clay. It is commercially known as Bentone 38 (Rheox Ltd) and is understood to be a dimethyl dialkyl ammonium hectorite clay.

1.2 Clay Mineralogy

The earth's crustal rocks and breakdown products (soils, clays and sands) are composed almost entirely of silicate minerals and silica. Oxygen, silicon and aluminium are the most common elements in the crust. Clays are distinctive in at least two properties making them technically useful: plasticity and composition. The term plasticity refers to the property of moistened material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed. Clay minerals are composed of extremely fine crystals or particles, often colloidal in size and usually plate-like in shape. The very fine particles yield very large surface areas that are physically sorptive and chemically surface reactive. Many clay minerals carry an excess negative electric charge owing to internal substitution by lower valency cations which, thereby increases internal reactivity in chemical combination and ion-exchange.

1.2.1 The Clay Mineral Concept

Since the late 19th century, scientists proposed that clay materials were composed of extremely small particles of a limited number of crystalline minerals (Le Châtelier 1887, Lowenstein 1909). This was known as the *clay mineral concept*. It was not until after the 1920's that adequate analytical techniques could provide positive evidence for the hypothesis. Hadding (1923) and Rinne (1924) were the first to publish X-ray diffraction analyses of clay materials providing evidence that in the main, clays were composed of crystalline materials. This work was complemented by Ross and Kerr (1931) who pioneered optical techniques to confirm that the components of clay materials were primarily crystalline. They also confirmed that the crystalline components were composed of an extremely limited number of chemical entities.

Pauling (1930) published results of his X-ray diffraction studies of various clays. Here he showed that clays, despite having different chemical compositions, are remarkably similar in structure. Pauling concluded that these minerals have a layer structure.

The clay minerals are essentially hydrous aluminium silicates in which magnesium or iron may, in whole or part, substitute the aluminium. In some minerals, alkalis or alkaline earth metals may be present as essential constituents. It is the components of clay minerals that largely determine the clays properties. Properties may also be influenced if non-clay minerals are present in appreciable amounts.

1.2.2 Classification of Clay Minerals

Type	Group	Sub Group	Species
1:1	Kaolinite	Dioctahedral	*Kaolinite, Halloysite*
2:1	Pyrophillite	Dioctahedral	*Pyrophillite*
	Talc	Trioctahedral	*Talc*
	Smectite	Dioctahedral	*Montmorillonite, Beidellite*
		Trioctahedral	*Saponite, Hectorite*
	Mica	Dioctahedral	*Muscovite*
		Trioctahedral	*Biotite*

Table 1.1: Classification of Clay Minerals
(Nomenclature Committee, The Clay Mineral Society)

Clays are often referred to as *layer silicates* or *phyllosilicates* since they are essentially composed of layers formed by condensation of linked tetrahedral (silica) sheets with linked octahedral $M_{2-3}(OH)_6$ sheets where M is either divalent (magnesia) or trivalent (alumina).

Table 1 shows a simple classification for 1:1 and 2:1 layer silicates giving examples of the more common species. Condensation in a 1:1 proportion gives rise to the 2 sheet or dimorphic minerals known as kaolinite. The 3 sheet or trimorphic clays are formed by a 2:1 condensation where the octahedral sheet is sandwiched between 2 inward pointing tetrahedral sheets.

1.2.3 Structural Principles of Clay Minerals

Most clay minerals are composed of two structural units - a tetrahedral (silica) sheet and an octahedral (alumina or magnesia) sheet.

In the silicon-oxygen sheet, the silicon atoms are coordinated with four oxygen atoms. Assuming no distortions, the oxygen atoms are located on the four corners of a regular tetrahedron with the silicon atom in the centre (Figure 1.1).

Figure 1.1 : Tetrahedral arrangement of Si and O

These units can exist as discrete entities or can combine by corner sharing O atoms. The silica tetrahedral groups are arranged to form a hexagonal network that is repeated indefinitely to form a sheet. Holes are observed in the hexagonal symmetry as shown in the figure below. The tetrahedrons are arranged such that the tips point in the same direction and the bases of the tetrahedron are in the same plane (Figure 1.2).

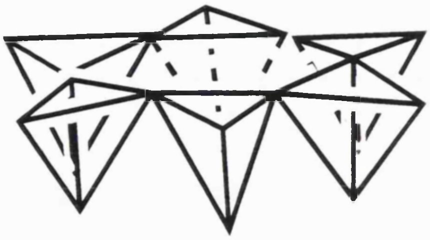


Figure 1.2 : Sketch of tetrahedral linking

In the alumina/magnesia sheet, Al or Mg is coordinated with six oxygen or OH groups. These are located around the Al or Mg atoms with their centres on the six corners of a regular octahedron. The oxygen atoms and hydroxyl groups lie in two parallel planes with the Al or Mg between the planes. The projection of the sheet shows that the oxygen and hydroxyl groups form hexagonal close packing (Figure 1.3).

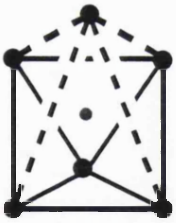


Figure 1.3 : Octahedral arrangement of Al or Mg with O or OH

The analogous symmetry and almost identical dimensions in tetrahedral and octahedral sheets allows the sharing of O atoms between layers. The fourth O atom protruding from the tetrahedral arrangement may be shared by the octahedral sheet.

1.2.4 Structural Properties of 2:1 Type Minerals

The 2:1 group minerals are composed of two silica tetrahedral sheets positioned on either side of an octahedral sheet. The tetrahedral sheet and octahedral sheet combine such that the tips of the tetrahedron silica layer and one hydroxyl group of the octahedral layer combine to form a common layer continuous in the *a* and *b* direction and stacked in the *c* direction.

Most investigations into the structural principles of 2:1 type minerals have focused on the dioctahedral smectites (e.g. montmorillonite). The currently accepted structure of the smectite minerals originates from the suggestions made by Hofmann et al (1933) and is based on its similarity to electrostatically neutral *pyrophillite* (Figure 1.4). This structure is termed dioctahedral since two of the three possible octahedral positions are occupied by trivalent aluminium atoms. If all of the three octahedral positions are occupied with divalent magnesium atoms, the structure is known as trioctahedral. This is represented by electrically neutral mineral *talc*.

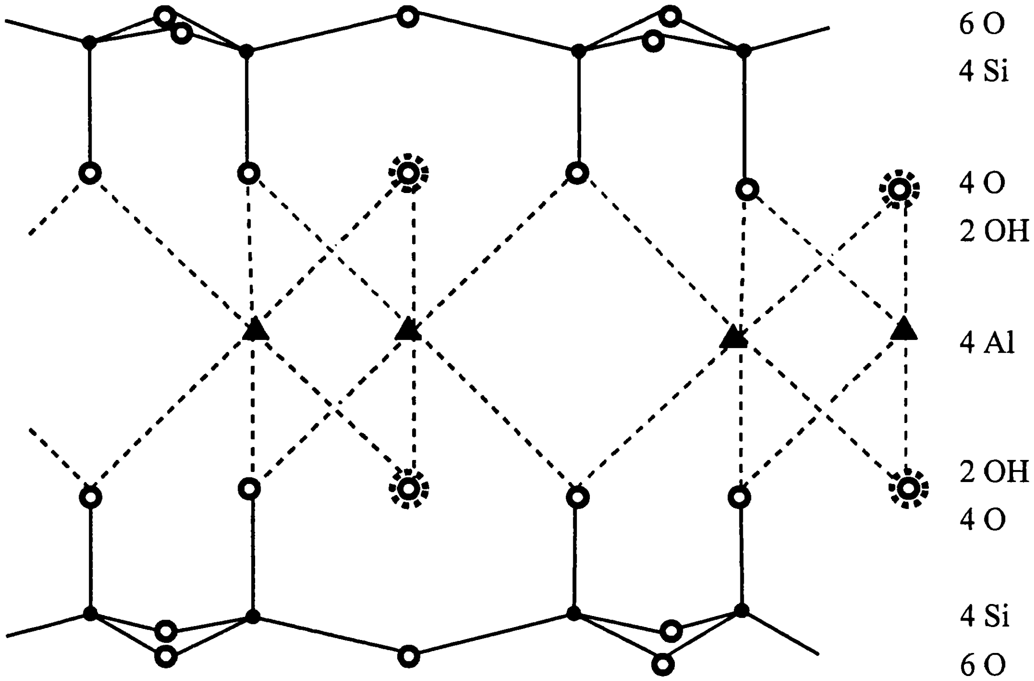


Figure 1.4 : The structure of pyrophillite

The 2:1 smectite minerals are derived from the prototypes of pyrophillite and talc through substitution of higher valence atoms for lower valence atoms e.g. trivalent Al may be replaced with divalent atoms (e.g. Mg/Fe) without filling completely the third vacant orbital. The result of incomplete filling of orbitals is an excess surface charge that is compensated by the adsorptions of surface layer cations e.g. Na^+, Ca^{2+} that are too large to be accommodated in the internal lattice (see Figure 1.5). This theory was first proposed by Marshall (1935), Hofmann (1933) and Hendricks (1942) and was confirmed using the technique of X-ray diffraction.

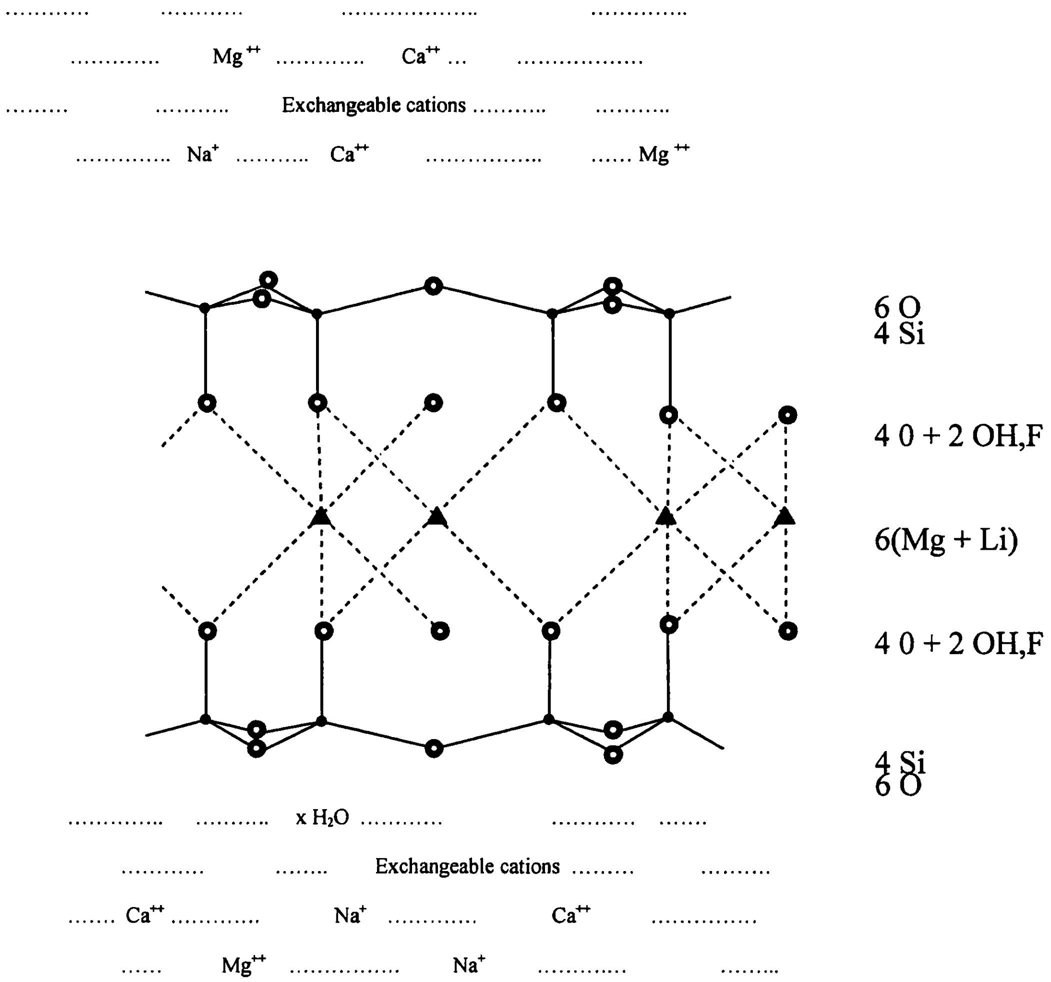


Figure 1.5 : The structure and chemical composition of hectorite

In the parallel stacking of the 2:1 units oxygen layers of each unit are adjacent to oxygen layers of neighbouring units. Weak forces of attraction between layers are primarily electrostatic van der Waals forces of attraction (Giese, 1975). Consequently the bonds are easily cleaved. This fact accounts for why these minerals occur in the form of flakes and are frequently described as plate-like or platelets, stacked like a deck of cards.

The most notable feature attributed to the structure of the 2:1 minerals is that water and polar molecules are able to penetrate between the unit layers causing the lattice to expand in the *c* direction. Barshad (1952) noted that *c* axis expansion was greater the larger the dipole moment of the reacting liquid but found no clear relationship with dielectric constant. Foster (1953) found that with sodium saturated montmorillonite, the degree of swelling bore no relation with cation exchange capacity or with tetrahedral substitution, however he found that there was a dependent correlation with octahedral substitution. To corroborate this finding Hofmann et al (1956) showed that the absence of charge as with mica and pyrophillite yielded no intercrystalline swelling.

1.2.5 Clay Charge

Clay particles carry a net negative charge due to a deficit of positive ions as described earlier. In the dry state, the excess of negative layer charge is compensated by the adsorption on the layer surface of cations too large to be accommodated in the interior of the crystal thus electrical neutrality is maintained. When clay particles are placed in water, these cations are subject to diffuse away from the layer due to the concentration gradient of the bulk solution. At the same time, electrostatic forces attract cations to the surface of the particles. The result is the build up of a distribution of compensating cations in a diffuse *electrical double layer* on the outer surfaces of the clay platelets.

1.2.6 Charge on the Face of Clay Minerals

Studies have shown that clay minerals carry a net negative charge on surface faces. There are a number of explanations to account for this net negative charge. The literature does not favour one particular theory but suggests a combination of the following factors - isomorphous substitution, lattice imperfections, broken bonds at the edges of particles and exposed hydroxyls. A brief description is given for each.

Van Olphen (1963, 1991) reports that the principle source of the observed negative charge on the flat surfaces of clay minerals is isomorphous substitution. An excess negative charge may also be accounted for by replacing higher valency atoms with lower valency atoms. That is, divalent atoms substituting trivalent atoms or univalent atoms substituting divalent atoms e.g. in the tetrahedral sheet, Si^{4+} may be partly replaced by Al^{3+}; in the octahedral sheet, there may be replacement of Al^{3+} by Mg^{2+} or Fe^{2+} without complete filling of the third vacant octahedral position. The small size of these atoms permits them to substitute the positions of Si and Al, hence the term *isomorphous substitution.*

Negative surface charge may also be attributed to crystal imperfections e.g. the absence of a constituent metal atom from its place in the crystal structure. Other imperfections thought to contribute to negative charge include localised bond breakages and dislocation of atoms. Such imperfections are difficult to measure analytically as the size of the effect would be negligible when analysing the clay mineral as a whole.

The dissociation of structural hydroxyls is another possible source of negative charge however, since structural hydroxyls are strongly bonded to aluminium or magnesium atoms in the lattice structure this theory is not generally considered. It is usually accepted that the electric double layer on the face surface of clay is constantly charged and dependent on the type and degree of isomorphous substitution and independent of electrolytes in the suspensions (van Olphen, 1963,1991).

1.2.7 Charge on the Edge of Clay Minerals

The atomic structure of edge surfaces is completely different to the face surfaces of clays. It follows that the electric double layer may also be different.

It is also possible that broken bonds at the edges of particles may contribute to the overall negative charge on the lattice. There is strong evidence to indicate that the edges of clay particles in fact carry positive charges in certain conditions (Thiessen 1942, 1947). An electric double layer is created on the edges of particles by adsorption of potential-determining ions (hydrogen and hydroxyl ions) when primary bonds are broken in the tetrahedral and octahedral sheets. The edge surface carries a positive double layer with the metal ions acting as potential-determining ions in acid solution. (Figure 1.6)

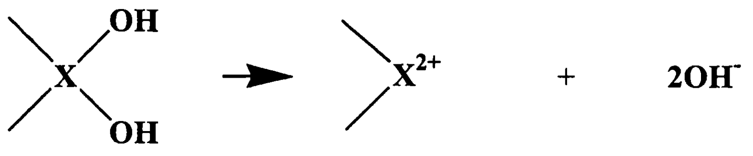


Figure 1.6 : Creation of potential-determining ions

In alkaline solution, the edge carries a negative charge with hydroxyl ions acting as potential-determining ions. The point of zero charge does not necessarily occur at neutral pH.

The tetrahedral silica edge surface of the clay particle normally carries a negative charge however it is known to carry a greater positive charge in the presence of aluminium ions. It is also thought that the silica sheets break at places where aluminium ions have been substituted.

In conclusion, under appropriate conditions, the entire surface edge may carry a net positive double layer and clay minerals show an anion capacity under certain conditions e.g. a kaolinite shows a small anion adsorption capacity in slightly acidic conditions but not in alkaline conditions.

Van Olphen (1963, 1991) cites an experiment performed by Thiessen (1942, 1947) that provides evidence of a positively charged clay edge surface. Thiessen mixed a kaolinite sol and a negative gold sol and prepared an electron micrograph of the mixture. It appeared that the small negatively charged gold particles were exclusively adsorbed at the edges of the kaolinite plates. Thiessen did not interpret the micrographs to be an indication of a positive edge charge on the clay, but rather he concluded crystal edges to be areas of higher adsorptive activity. It is more likely that the preferred edge attachment of gold particles is a result of mutual flocculation of the negative gold particles and positive kaolinite edges.

1.3 Properties of Hydrophilic Clays

1.3.1 Ion Exchange

The compensating cations on the flat layer surfaces of clay minerals may be easily exchanged by other cations when available in solution. These are commonly known as 'exchangeable cations'. It may be generalised that cation exchange increases with:

a) decreasing hydrated radius and increasing polarisability
b) increasing counter-ion charge
c) decreasing ease of cation hydration

In agreement with the above criteria the association of counter-ions with montmorillonites is generally in the order:

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+}.$$

Exchangeable cations are located on the external surfaces of the aggregate and between the unit layers. The total amount of these cations may be determined analytically and are expressed in milliequivalents per 100g of dry clay. This is known as the *cation exchange capacity* (CEC) of the clay. The presence of the exchangeable cations causes a slight increase in the basal spacing compared to that of the prototype model, pyrophillite (from ~0.913nm to >0.96nm for dry clay). The basal spacing is the distance between a certain plane in a layer and the corresponding plane in the next layer. This is also known as *001* or *c spacing.* Basal spacing is determined by the size of the compensating cation and is often found to be less than the diameter of the compensating cation. One explanation for this is that the cations are partially sunk in the hexagonal holes of the tetrahedral sheet.

The strong negative charge of the faces of the clay minerals repels anions but they are attracted to the weakly positive charge on the clay edges. Anions can also specifically bond to cations on the clay mineral surface. Adsorption of fluorine ions is commonly found in trace amounts on the edge surfaces of hectorite minerals.

1.3.2 Hydration of Smectite Clay in Water

Within the lattice structure of stacked smectite platelets, layers of water molecules coat the silicate units even when the clay has been air-dried. There are two principal methods in which clay particles may be hydrated. Firstly, hydration may occur at the surface of the crystal lattice. The 2:1 minerals present two siloxane surfaces capable of interaction with water molecules. Secondly, the counter-ions may be hydrated. Water adsorbed onto the surfaces of the clay minerals appears to retain the properties of liquid water i.e. it exhibits similar water tension, its infrared spectrum resembles that of liquid water and it dissolves both organic and inorganic species and allows diffusion.

Water molecules consist of V-shaped arrangements and have bond angles of 104.5° (close to a tetrahedron). On account of the lone pairs of electrons situated above and below the oxygen nucleus, a water molecule may be described as resembling a tetrahedron with two positive and two negative corners. Consequently a water molecule has a dipole moment.

When two water molecules approach each other, there is electrostatic attraction between the positive tetrahedral corner of one molecule and the negative tetrahedral corner of the other i.e. there is an electrical interaction between the proton and the lone electron pair. Since the proton of hydrogen is involved, the bond created is called the hydrogen bond. It is not certain how water is bonded to the surface of the clay. It is believed that water molecules adjacent to the clay surface are bonded to the oxygen atoms of the surface layer by covalent hydrogen bonding.

1.3.3 Swelling of Clays

X-ray studies indicate that when clays are contacted with water or water vapour the distance between adjacent layers increases in a stepwise manner. It was concluded that water molecules penetrate between the layers and are adsorbed in successive monolayers. This is known as *interlayer swelling* and an increase of basal spacing of the clay can range between the order of 1.25 - 2.0 nm. The second stage of swelling is due to the repulsion of the double-layers which forces the platelets further apart. It is the dissociation of some of the cations in aqueous solution that gives rise to the double-layer repulsion. The thickness of the water layers between silicate units depends on the nature of the exchangeable cation at a given water vapour pressure - an increase in counter-ion charge increases the amount of water adsorbed. For example, under ordinary conditions a smectite with Na^+ as the exchange ion frequently has one molecular water layer and a basal spacing of ~1.25 nm. With Ca^{2+} there are frequently two molecular water layers and a basal spacing from about 1.45 - 1.55 nm.

It would appear that the thickness of the water layers between successive silicate layers is an integral number of molecules i.e. one, two, three etc. molecular water layer thick (Bradley et al, 1937). When several layers of water are present osmotic forces caused by relatively high ionic concentrations increase swelling further. Swelling is dependant upon osmotic and hydration forces overcoming the attractive forces.

1.3.4 Particle Association

There are three forms of particle association that may occur in an aqueous suspension when clay platelets flocculate: face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE). The physical results of the three types of association are quite different. Face-to-face association leads to multilayer stacks of platelets, frequently called *aggregations*, with dimensions similar to those of unassociated unit layers. The major difference is the difference in thickness of the platelet. The splitting or delamination of FF associated aggregates into individual plates are described as *dispersion* of the clay. When dispersed, the individual plates so produced are thought to interact through EF and EE associations to form an open 3-dimensional *House of Cards* structure (Figure 1.7). The structure extends throughout the aqueous phase imparting gel-like properties. Associations as described above are attributed to attractions between the oppositely charged edges and faces of the clay platelets and/or minimisation of the double layer repulsion between the negatively charged faces.

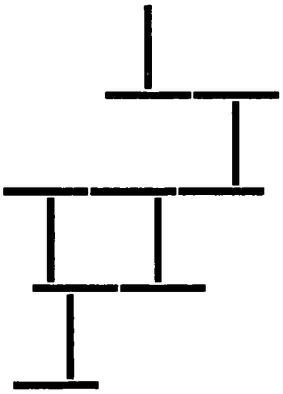


Figure 1.7 : Edge-to-face association (House of Cards)

The 'house of cards' phenomenon has been predicted for many years, in particular Van Olphen (1963, 1991) discusses in detail the 'house of cards' model. It is only in recent years that Zou and Pierre (1992) and Gu and Doner (1992) have provided visual evidence (SEM and freeze fracture TEM respectively) of the presence of the 'T' and 'H' shaped structure elements that comprise a 'House of Cards'. Some degree of scepticism should be taken regarding this theory since these SEM and TEM micrographs indicate that only certain domains of the microstructure to be of this order, i.e. it is not a continuous structure throughout the samples and therefore the description 'house of cards' type microstructure is not truly representative.

1.4 Hydrophobic Clay Chemistry

1.4.1 Organic-Clay Interactions

Studies into clay-organic species began in the 1930s. Evidence to show that the reaction was one of ion-exchange was given by Smith (1936) when he reacted organic bases and their salts with montmorillonites. It was Gieseking and colleagues who showed definitively that organic ions enter into cation-exchange reactions with the clay minerals, particularly the smectite group (Gieseking, 1939; Ensminger & Gieseking, 1939, 1941).

Many common organic cations contain basic amino groups and it is the reaction between these compounds and the clay minerals that has been studied in the most detail. These cations are ammonium ions in which one or more of the hydrogens have been substituted by organic groups. Such cations are also known as *onium* ions. Other onium ions that also replace cations include phosphonium, sulphonium and oxonium ions.

There are a number of ways organic molecules may be associated with clay particles depending on the reacting species e.g. a molecule may be absorbed on the clay lattice by ion-dipole forces, by van der Waals forces of attraction or by hydrogen bonding. It may also form a complex with a counter-ion of the clay or, if it has ionised, may undergo ion exchange with the original counter-ion.

1.4.2 Ammonium Ion Reactions with Montmorillonite

The adsorption of organic cations by montmorillonites is influenced by both electrostatic (Coulombic) and by van der Waals forces. In general, larger ions are more strongly adsorbed due to greater forces of attraction and because it is virtually impossible for smaller ions to replace them. Grim *et al.*(1947) confirmed that van der Waals forces influenced the adsorption of large organic cations by clays when uptake was found to exceed the cation exchange capacity. The amount of organic ion adsorbed varies with its orientation on the clay-mineral surface as well as its size. Smaller organic ions even when present in excess did not exceed the cation exchange capacity of the clay. McAtee (1959) showed that sodium is more easily replaced than calcium or magnesium on montmorillonites. The exchange of sodium is stoichiometric whereas calcium and magnesium may only be partially exchanged. It is thought that it is because of the larger groups of flocculated clay in calcium and magnesium systems that cations cannot effectively exchange onto the clay surface or even has enough room to adsorb effectively. McAtee indicates that the cations on hectorites are easier to replace than cations on other montmorillonites. The author suggests this is because the charge on the crystal lattice is a consequence of replacements within only the octahedral part of the hectorite structure as opposed to replacements in both the tetrahedral and octahedral layers of other montmorillonites.

According to Weiss (1963), the bond strengths of the alkyl compounds decrease sharply in the series RNH_3^+, $R_2NH_2^+$ and R_3NH^+. Quaternary alkyl ammonium ions R_4N^+ behave quite differently; asymmetrical ions such as dimethyl dialkyl ammonium ions are classified among the primary ammonium ions whereas symmetrical ions rank behind the secondary ammonium ions. The exchange process can be represented by the following relationship:

$$\mathbf{Na^+_{clay} + R_4N^+_{soln} \Rightarrow R_4N^+_{clay} + Na^+_{soln}}$$

The adsorption of organic ions on the basal plane surface of montmorillonite is shown conclusively using X-ray diffraction by measuring the shift in the basal spacing of the clay units accompanying the reaction.

1.4.3 Orientation of Organic Ions on Clay Surfaces

Organic ions are orientated between the montmorillonite layers so as to cause the minimum expansion of the layers (Hendricks, 1941). Alkyl chains of primary ammonium groups are thought to lie parallel to the flat surfaces of montmorillonite. When organic chains occupy more than half the available area per exchange position, the organic molecules on the top surface of one layer fit into the gaps between those of the bottom surface of the layer directly above it. The resulting separation between layers is therefore the thickness of one chain (~0.4 nm). When the chains occupy more than 50 percent of the surface area per exchange position, adjacent laminae are unable to approach as closely and a thickness of two hydrocarbon chains is observed (~0.8 nm). Because of the tetrahedral arrangement of the quaternary alkyl ammonium ions the orientation of the alkyl groups cannot be deduced with any certainty from basal spacing of their respective complexes but the 'flattest possible' arrangement is indicated by XRD.

1.4.4 Properties of Organically Modified Montmorillonite

The most notable feature of montmorillonite after the replacement of inorganic cations initially present on the clay surface by organic species is the marked reduction in water uptake, first noticed by Gieseking (1939). He observed that montmorillonite complexes failed to show an increase in basal spacing when exposed to water vapour or liquid water and postulated that a large proportion of the clay surface being occupied by organic molecules would no longer be available to water. In addition, the alkyl groups of the cation would tend to repel rather than attract water molecules (Hendricks, 1941). Thus there is a transformation of the clay from hydrophilic to hydrophobic (organophilic) nature. Such transformations have led to the widespread use of clay complexes as thickeners and gelling agents for organic systems.

When dry clay is dispersed in a suspension containing organic species the hydrophilic nature of montmorillonite decreases as the inorganic cations initially present are progressively replaced with organic ions. A minimum point is reached near the exchange capacity beyond which the system behaves as a positively charged hydrophobic colloid. Properties of the clay show an inversion or reversal at this *equivalence point.* For example, the viscosity of aqueous sodium-montmorillonite increases to a maximum at this point and then declines when increasing amounts of ammonium ions in solution are added. The initial increase in viscosity is attributed to flocculation of montmorillonite particles brought about by a reduction in repulsive interaction between silicate layers and consequently the diffuse double layers collapse. Beyond the exchange capacity, the clay particles now coated with a layer of close packed positively charged ions will repel each other and deflocculation occurs. (van Olphen, 1991)

1.4.5 Swelling of Organically Modified Clays

Swelling of montmorillonite complexes was examined by Jordan (1949). He showed that organophilic properties were negligible until an amine with a chain of 10 carbon atoms is reached. The swelling of dodecylamine complexes in liquids of nonpolar nature (aliphatic or aromatic hydrocarbons) is low and gel volume increases with the dielectric constant of the liquid although correlation is not perfect. Jordan also found that, for complexes prepared with single-chain primary amines of less than sufficient size to coat the montmorillonite particles completely with a layer of hydrocarbon chains, swelling can be developed in nonpolar hydrocarbons if a second organic liquid or *polar additive* e.g. an alcohol, ester, ketone or aldehyde is added to the system. An increase in swelling can be indicated by an increase in system viscosity. It was postulated that the highly polar additive is adsorbed onto the uncoated surface of the montmorillonite, thereby rendering the individual platelets entirely organophilic and compatible with the hydrocarbon portion of the solvating liquid.

Jordan (1949) showed that montmorillonite complexes with quaternary ammonium salts having two long aliphatic chains are organophilic in single hydrocarbon liquid systems. Dispersion takes place much more readily with the double chain complexes than with the single chain complexes probably because the completely coated particles are more compatible with the hydrocarbon. In the case of double chain complexes, there is a tendency for an initially greater separation of the montmorillonite units than in single chain complexes.

The author concluded that the swelling process involves two factors for an incompletely coated clay complex:

1) high adsorption energy of liquid for uncoated clay
2) high solvation energy of liquid for organic coating

Adsorption of polar molecules by the clay must tend to separate the plates therefore rendering the particle more organophilic and the organic coating more accessible.

1.4.6 Dispersion of Organoclay Platelets in Organic Media

Organoclays form agglomerates of stacked platelets. This is due to the layers of quaternary ammonium compound on the surfaces of the clay that have an affinity to agglomerate through van der Waals forces of attraction and Coulombic forces. In order for organoclays to function optimally as rheological modifiers, it is necessary to delaminate the agglomerates. This is known as *dispersion.* Dispersion is the physical process in which the stacked platelets of the organoclay are separated in a fluid system. Through dispersion, the individual platelets build to form a structured network with a vast solid surface area to volume of liquid ratio. It is this phenomenon that is responsible for rheological changes.

Dispersion of organically modified clays in organic media is related to swelling and gelation. Jordan (1949) accounts for the increase in bulk observed when clays are saturated with organic liquid, to be attributed to surface binding of organic liquid to the surface of the clay. The cohesive forces between the clay platelets are relatively high and must be overcome in the process of swelling. In order for swelling to occur, the organic liquid must penetrate between adjacent platelets and force them apart thus forming a layer of liquid around each discrete platelet. An increase in viscosity is observed and the system is seen to gel. The definition of gelation is as follows: a process whereby a solvent is mechanically trapped within a network and the whole system resembles a solid appearance.

The process of gelation is currently not defined, however the proposed mechanism as suggested by Rheox Ltd (Rheox Ltd, Rheology Handbook) is commonly accepted to be correct and to date has not been challenged. The mechanism is a three-stage process. Firstly agglomerated clay is broken down to smaller agglomerates by stirring. The action of shear breaks down larger agglomerates. Stage two involves the addition of a polar activator that is said to penetrate between the clay platelets and cause swelling. Jordan (1949) describes a 'hair brush' analogy to account for swelling. Alkyl chains attached to the clay through ion exchange are believed to lie flat to the clay face surface in dry material. The cohesive forces between platelet and adsorptive forces holding the alkyl chain to the mineral surface render it difficult for the solvating liquid to separate the flakes and solvate the attached chains. It is believed the compounds in the solvating liquid would be absorbed more strongly than the alkyl chains to the clay surface and therefore more likely to displace the alkyl chains out away from the surface to create the effect of hairbrush bristles.

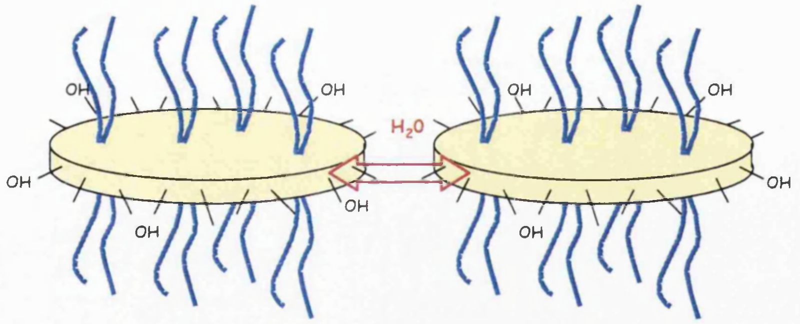


Figure 1.8 : Platelet edges bridged by water molecules

The effect of swelling reduces the intermolecular forces of attraction between platelets. The third stage is to incorporate a degree of shear to the mixture to break these forces of attraction and delaminate the particles to their primary state. The gelled microstructure is accounted for by Magauran et al (1986), who propose that structuring or gelation of the organoclay is developed by edge-to-edge hydrogen bonding between hydroxyl groups on the organoclay platelet edges. They suggest that water molecules bridge hydroxyl groups on adjacent organoclay platelet edges (Figure 1.8).

1.5 Factors that Effect Microstructure and Gel Formation

In order to understand the microstructure of an organoclay gel, it is necessary to determine whether the mechanism proposed by Rheox Ltd for creating a gel is accurate or more specifically, whether each stage is essential. It is not clear from any of the literature sources what exactly is meant by 'shear' and therefore it is important to qualify and quantify this. It is also important to understand the role of the polar activator and to determine whether its part in the mechanism is truly for structuring, aiding swelling or stability and if it is an essential component.

In order to determine this, it is important to firstly have a good understanding of the chemical composition of the organoclay under investigation. Then, it is necessary to look at the different conditions that may impart a physical effect on the nature of clay. There are three key areas that could impart major effects on the microstructure of organoclay:

- Polar additive (chemical energy)
- Temperature (thermal energy)
- Shear (mechanical energy)

1.5.1 Polar Additives

1.5.1.1 Description of Polar Activators

Polar activators are chemical species that are added to the organoclay solvent mixture in the early stages of processing. The addition of polar ingredients to the organoclay formulations is believed to enable dispersion and contribute to the formation of hydrogen bonds between platelet edges. They are believed to target the surface of clays and intercalate between the platelet layers to cause a swelling effect. The affinity of the polar active ingredient to the clay surfaces disturbs the van der Waals forces of attraction between platelets thus enabling dispersion through shear.

The polar ingredients are usually low molecular weight compounds that carry a dipole moment. The most common polar activators recommended in the trade include propylene carbonate, methanol, ethanol and acetophenone. Trade literature also recommends that 5% water is added to polar activators, in particular, to alcohols to maximise dispersion. Water is said to affect the dissociation of the surface groups of clay and hence alter the surface potential, surface conductance and ultimately the stability of the system. (Moraru et al,1980)

There is a vast range of polar additives available to perform the requirements of a chemical activator e.g. methanol, ethanol, propylene carbonate, acetone. Water is not quoted as a viable option in its own right as a polar activator despite it being a highly polar species, however it is frequently stated that it is required at a low percentage in conjunction with a polar activator in order for gelation to occur. This again is an anomaly since the literature does not quote anhydrous properties of the polar activators under investigation and therefore it should be presumed that trace water would always be evident in standard chemicals. It should also be noted that much of the literature supplied is trade literature e.g. Rheox, Laporte and therefore much of the work is performed to optimise their clay for a specific technology e.g. paint industry. Consequently, the information supplied can tend to be rather biased and sometimes lacking relevant data to substantiate claims.

1.5.1.2 The Role of the Polar Additive

There are many references that suggest that the role of the polar additive is to have an effect on swelling of clay platelets, dispersion and gel network formation. It is suggested that polar activator intercalates between the clay platelets causing swelling. This is processed using shear (not quantified) that causes the platelets to disperse in the liquid medium. Evidence of this procedure is given by X-ray diffraction and Infra-red spectroscopy data. (Shaefer et al, 1971; Cody and Reichert, 1986; Kemnetz et al, 1989) Using the data from these two techniques, it is claimed that polar activators are *essential* to disperse clays efficiently. From X-ray diffraction experiments they state that an increase in basal spacing between clay platelets followed by absence of peaks provides evidence that a fully dispersed system has been created. Whereas a narrowing of band-width for the silicate bands again indicates optimal dispersion. Their experiments are based only on systems that contain polar activators and claim that it is due to their presence dispersion occurs. There are no comparative studies of systems without polar activators to truly substantiate these claims. The authors concede that polar activators operate optimally when incorporated with mechanical energy.

Mention of fully dispersed clays is frequently quoted in the literature, although, evidence of a fully dispersed system by techniques such as optical imaging or particle sizing is negligible. Since there is so little data to substantiate such claims it would prudent to hypothesise that it is unlikely that an optimum dispersion is ever managed using the methodologies described and therefore caution must be taken when applying the information taken from the literature. The method of dispersing clay in the organic media ranges from low shear mechanical stirring for a period of approximately 30 minutes to using standard dispersion blades. Consequently, the claims of the functions of polar activators made in the literature must now be taken with some degree of caution since there is no certainty that the effect of the polar activator functions on agglomerates or on individual platelets. Nevertheless, provided that this is accounted for when considering prior work it is possible to gain some understanding of the function and role of the polar activators in organoclay chemistry.

1.5.1.3 The Interaction of Polar Activator and Organoclay

According to Rheox Ltd. the polar additive serves two purposes:

1) it delaminates the organic-clay
2) it carries water into the hydrophobic system

The polar activator is said to migrate to the faces of the platelets where, "because of its size, forces the layers apart" (Rheox Ltd Manual). The increase in basal spacing weakens the van der Waals forces of attraction between platelets. With the aid of mechanical energy the van der Waals forces are overcome and the platelets separate. Water carried into the system by the polar additive migrates to the platelet edges where hydrogen bonding with hydroxyl groups occurs.

If insufficient polar activator is added to the system a partial delamination of platelets occurs and an inadequate gel is formed. If there is excess, the polar activator migrates to the platelet edges and interferes with the hydrogen bonding and thus there is a reduction in gel network structure. The recommended levels of polar activator in combination with Bentone 38 are illustrated in Table 1.2 (reproduced from Rheox Ltd Manual).

Chemical Polar Activator	% based on weight of Bentone
Methanol/water (95/5)	33
Ethanol/water (95/5)	50
Propylene Carbonate	33
Propylene Carbonate/water (95/5)	33
Acetone/water (95/5)	60

Table 1.2 : Recommended levels of polar activator relative to percentage of clay

The role of the polar additive in the preparation of clay dispersions was also described in the literature as follows: Polar activators have a common feature - the presence of functional groups such as hydroxyls and carbonyls which are available for hydrogen bonding. The role of the polar activator in the formation or disruption of hydrogen bonds is currently not understood. It would be expected that any chemical species that contained functional groups could be used as polar additives providing the species was sufficiently soluble in the solvent. It would appear that not all chemical species with the aforesaid functional groups serve as efficient polar activators and thus play a less effective role in network formation (Magauran et al, 1986).

Little work has been done in investigating which type of polar activator is the most effective and it has been very much of the rationale that 'this one works'. It is suggested that functional groups may be responsible for effective dispersion or gelation, but not necessarily the two modes combined. For example, the carbonyl compounds (such as propylene carbonate) seem to be efficient at dispersing agglomerates but do not effectively form gels, however, chemical additives that possess the hydroxyl functional group appear to provide better gelation properties. For both examples, it is claimed that when trace amounts of water are added efficient gelation will occur (Magauran et al, 1987).

It is likely that the size of the molecule is critical to the effectiveness of a polar acivator in its role in intercalation of clay platelets (Gherardi et al, 1996). Gherardi and colleagues determined that interaction of polar activators (alcohols) with a trioctahedral organoclay alters the surface properties of the clay. Their experiments showed that there was a sol/gel transition at a concentration of 11% clay in the absence of polar activator, however, when polar alcohol (ethanol or methanol) was added, this transition could occur at lower concentrations. The suggestion for the higher chain length alcohols not contributing to gelling was that it was likely that the solvent had a greater affinity for the polar molecules than the surface of the clay. It is however more likely that the size of the molecules hindering intercalation that had a greater influence. Nevertheless the work corroborates many authors' work that vindicates lower order alcohols as effective polar activators.

1.5.1.4 Polar Activator Optimisation

There are many publications detailing the amount and type of polar activator that is required for organoclay dispersion and gelation, however this information is mainly supplied in the form of trade literature for specific product development in areas such as the paint industry (Rheox Ltd, Laporte Manual). It is postulated that once an optimum dispersion is achieved, polar activator may act as a degellant and cause a loss in viscosity. (Magauran et al, 1986; Mardis, 1984; Kieke and Nash 1983; Cody and Reichert, 1986). Figure 1.9 shows a graph of the optimum levels of polar activator and is reproduced from the literature (Magauran et al, 1986).

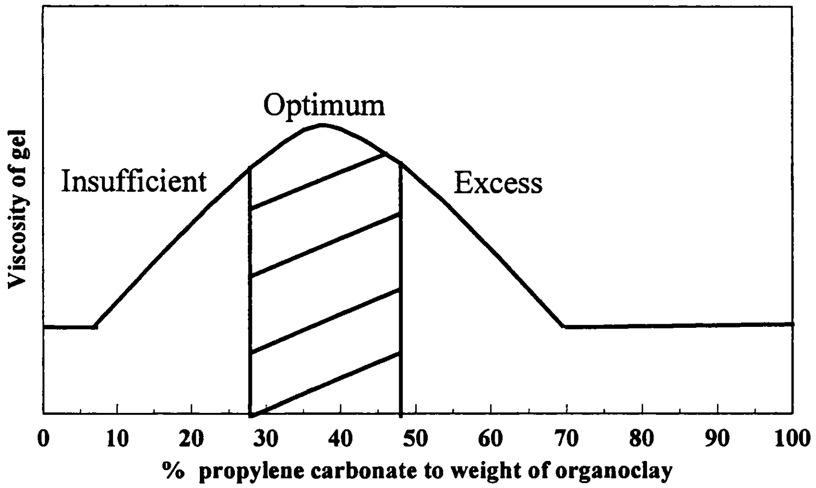


Figure 1.9 : The influence of polar activator on clay gel strength (reproduced from Rheox Manual)

The optimum amount of propylene carbonate is quoted as 30-50% by weight of clay (Magauran et al, 1986). However, it is believed this was developed for grease/paint systems and in fact the actual solvent systems used needs to be looked at in conjunction with the level of polar activator as this will determine specific intermolecular interactions and hence final properties of the system.

The effectiveness of polar additive is also thought to be influenced by its solubility in organic medium. When water (0.1%) was added to a dispersed but not gelled system gelation was seen to rapidly occur. Water was chosen as it forms hydrogen bonds and it is theorised that gelation results from the formation of hydrogen bond bridges between the edges of clay platelets. Water, having been found to promote gel formation in pre-dispersed systems, does not appear to cause dispersion. It is not understood why water should promote gelation at levels significantly lower than other activators (Cody and Reichert, 1986). Commercial polar activators tend to function well as both dispersants and gel promoters e.g. ethanol, methanol, acetone although it should be noted that all of these agents contain a small percentage of water.

The very fact that clays are species with surfaces that possess a huge affinity for ionic species combines well with the notion that polar chemicals will be attracted to the surface of the clay. It is this factor that was paramount to the development of the mechanism of dispersion and gelation as proposed by Rheox Ltd. It would also provide an explanation to the findings that Jordan and colleagues made in respect of the swelling of clays in organic media. (Jordan et al, 1949).

It is certainly true that the addition of polar molecules to clay slurries contributes to the increased viscosity of the bulk phase. It is not clear however exactly where or how the polar activator interacts with the organoclay to create this effect. Kieke et al, (1983) speculated that polar activators appear to have an affinity to the surface of the clay. They postulate that polar molecules are attracted to the clay surface that carries a net negative charge. Their belief is that the polar activator is able to penetrate between the platelet layers and position itself on the vacant O sites of the face of the platelet. This has an effect on the orientation of the alkyl chains of the surfactant quaternary ammonium that preferentially lie as parallel to the surface as possible (Hendricks, 1941). The effect is said to be a result of reorientation of the alkyl chains, through steric hindrance, up and away from the clay surface. This is based on evidence from X-ray diffraction by an increase in the basal spacing between platelets. (Kemnetz, 1989; Jones, 1983; Burba and McAtee, 1981) Through this intercalation, polar activators are deemed to be able to overcome the van der Waals forces of attraction that hold the clay platelets together (Lesshaft, 1967). The mode by which they influence gelation is believed to be through their contribution through hydrogen bonding between the hydroxyl groups at the edges of the platelets through edge to edge interactions. This is where the role of water is believed to play an important role and as mentioned earlier it is hypothesised that water is necessary to enable gelling (Jones 1983; Kieke et al,1983).

If it was true that intercalation of polar activator was possible and was responsible for swelling then it would be feasible that only a moderate amount of shear would be required to structure the clay particles and enable a gel network to form. Contrary to this school of thought, some believe that it is necessary to break down the large agglomerates to small agglomerates to enable interaction with clay surfaces (Cody and Reichert, 1986; Magauran et al, 1987). It is reasonable to question why should intercalation only occur in smaller agglomerates and it may be more pertinent to assume that the polar activator may only affect the exposed surfaces of the clay. If this were true, then the effects of gelation would be attributed to small agglomerates interacting together rather than primary particles.

1.5.2 Thermal Energy

Thermal energy is not cited in the literature as a potential method for delamination of organoclay platelets. It is inherent in all processes that impose work onto the system in the form of kinetic energy and it is technically very difficult to ever remove thermal effects when using a mechanical device that puts a great deal of work into a process. It is possible, however, to determine the effect of thermal energy alone on clay platelets.

1.5.2.1 Phase Transition of Quaternary Ammonium Chloride

The composition of an organoclay can be considered to be a mineral crystalline body that is coated with a quaternary ammonium compound. The quaternary ammonium compound is compacted closely to the surface of the organoclay face. The physical state of the hydrocarbon chains of the quaternary compound at room temperature would be that of a semi-solid gel (L_β) and rigid due to local ordering of chains i.e. molecules do not diffuse freely. The quaternary layer can be imagined as a sticky layer sandwiching two mineral layers of clay. By applying thermal energy to the system, the organic hydrocarbon layer on the surface of the clay would undergo a phase transition to the L_α (liquid) phase. In the L_α phase the molecules of the quaternary ammonium are fluid and molecules are free to diffuse. It is envisaged that the fluid layer between platelets would enable slippage of platelets across each other and with the aid of shear (in a lateral direction) clay platelets would be more readily delaminated.

The transition between the L_α and L_β is a first order transition and for quaternary ammonium compound derivatives of dihardened tallow this phase transition range would be expected to range between 45 and 60°C depending on the chain length of the hydrocarbon chains present. The majority of hydrocarbons of Bentone 38 would be expected to be C18 being a derivative of tallow. It should be considered that since tallow is derived from a natural source and not purified to a high grade it is feasible that a number of lower chain length hydrocarbons could be present as contaminants. These would be expected to be in reasonably low proportions compared to C18 hydrocarbons. Nonetheless, these lower chain hydrocarbons would undergo a phase transition at lower temperatures and account for the broad phase transition temperature range.

1.5.3 Mechanical Energy

The method of processing organoclay is an area where little prior work has been applied. Throughout the literature, reference is made to pieces of equipment, however there is little physical data to connect the effect of mechanical energy to structuring or gelating the organoclays. The open literature states that it is essential to use a polar activator in order to gelate an organoclay (Materson and Hahn, 1982) and, mechanical energy is required to ensure a full dispersion is achieved. It is certainly true that polar activators contribute to structuring but evidence that they are in fact essential is questionable. There is no evidence to show that polar activators alone, have the capability of overcoming the van der Waals forces of attraction between clay platelets and therefore it would be expected that a subsequent form of energy would be required to overcome these forces. It is therefore reasonable to assume that the literature is correct in stating mechanical energy is required.

The suppliers of Bentone 38 do not quantify the amount of mechanical energy required to ensure dispersion is achieved although recommended mixing times are quoted as mentioned later in Table 1.3 (Rheox Ltd). The supplier literature does not provide sufficient detail of the configurations of equipment utilised to enable calculation of tip speed, shear rates and so on. It has therefore been necessary to make assumptions in these fields.

The detail of the mechanics of processing organoclays is limited to supplier and trade literature and it is evident from later publications Laba (1993) that their methodologies are now regarded as correct. There is no physical data given in the literature to prove that complete delamination of platelets is achieved using any of the suggested processing equipment. The recommended processing equipment ranges from rotor/stator emulsifiers to homogenisers. There are no guidelines to which is more efficient and it would therefore be assumed that the processing equipment that exerts the lower shear rates (rotor/stator arrangement) would be sufficient to delaminate particles to generate a viscous medium.

A fully dispersed organoclay is one in which all agglomerate stacks of platelets have been delaminated into their primary particle state. Magauran et al (1986) claim that dispersion is associated with the effective incorporation of organoclay in the base oil by a combination of mechanical shear and chemical polar activation, while gelation is achieved when the dispersed platelets form a hydrogen-bonding network. To obtain a gel network of hydrogen-bonded organoclay platelets, a combination of chemical activation and mechanical shear is required (Rheox Ltd, Rheox Handbook).

The method described to achieve a maximum dispersion and gelate the organoclay is as follows:

- The organoclay suspension (clay and bulk liquid phase) and polar activator is first stirred using a drill press stirrer (450 rpm, 30 min)
- The resulting suspension is processed by multiple passes through a Tri-Homo Dispenser mill (0.003 inch gap, 230 g/min).

Altering the gap size between 0.001 inch and 0.009 inch was said to influence the hardness properties of the 'gel' when measured using a penetrometer. There is no data or reference to indicate that optimum dispersion was ever achieved and from the configurations quoted above it is impossible to determine what amount of shear the organoclay was subjected to. It has to be assumed that the shear rate experienced by the organoclay would be comparable to that of a conventional shear mixer (Silverson homogeniser L4R) (Baker, 1999).

Kieke (1986) goes into some more detail when he makes reference to the fact that the structure of clay is dependent upon the type of mechanical shear that is applied. He states that in order to achieve a 3-dimensional network for oil entrapment, a mill e.g. homogeniser, rotor-stator mill or a 3-roll mill provides turbulent shear that is necessary to yield a 3-D network. Kieke does not provide detail of gap dimensions, flow rates or other parameters for such mills that would enable calculation of shear rate or power to work ratios or in fact that shear was turbulent and not laminar.

Another method for dispersing organoclays is described by Cody and Reichert (1986). Here a Spex shatterbox is used. This is designed primarily as a grinding machine to pulverise samples. It consists of a solid metal carbide disk that oscillates back and forth within a circular metal carbide can. This motion is said to impart shear from the sliding of the disk and impact from collision of the puck and the retaining wall. The shear rate was not stated and no dimensions, or speeds were quoted to enable calculation. Degree of dispersion was measured using infra-red spectroscopy using the 1040cm^{-1} Si-O-Si band as a reference point. The authors claimed that the more the band-width narrowed, the greater the degree of dispersion. Following 60 minutes milling time the band-width narrowed slightly. One could argue that this does not provide sufficient evidence of complete dispersion. X-ray diffraction was also used to determine the basal spacing of organoclay. It was observed however, that no increase in basal spacing was observed for the samples that had been milled, even after 80 minutes milling time. This would suggest that the shatterbox method for processing organoclay does not provide sufficient shear to delaminate agglomerated clay.

The trade literature supplied with the organoclay (Rheox Ltd, 1996) provides the following information. Organoclay is usually supplied as a powder that needs high-energy mixing. Rheox provides four generic types of equipment suitable for delamination of clay platelets: impeller, rotor/stator, emulsifier, planetary mixer and homogenisation. The literature recommends that the highest speeds and the information would indicate that the same gelation would occur using an homogeniser compared to using a simple impeller stirrer. This would suggest that mechanical energy is not the driving force to delamination of particles, rather the support for incorporating the polar activator and enabling intrinsic mixing.

Thr specific detail of the mixing equipment is limited, however the literature indicates that the homogeniser used for experimental purposes is a bespoke homogeniser (Manton Gaulin, APV Homogenisers, Denmark). The Manton Gaulin homogenisers are designed primarily for use as emulsifiers, being used widely in the dairy industry. They are also recommended for uniformly dispersing solid particles through a liquid. The homogeniser consists basically of a positive displacement pump and a homogenising valve assembly. The pump forces the product under pressure through a small, adjustable gap between the valve seats and valve. This causes turbulence and intense extensional flow mixing. The Manton Gaulin homogenisers have an upper pressure limit of 700 bar. There are no details to describe the pressures used to manufacture gels on a Manton Gaulin or whether a single pass, multiple pass or continuous process was required. APV Homogenisers also manufacture a very high-pressure homogeniser known as the Rannie homogenisers. These homogenisers have an upper pressure limit of 2000 bar. The homogenising valve assemblies are the same for the equipment models in both ranges. There is no reference made in the open literature to the very high pressure Rannie homogeniser being used for processing organoclays.

One point worth noting is that the distinction between mechanical and thermal energy is practically impossible to achieve since the work performed through mechanical energy is transformed as heat energy.

1.5.4 Microstructure of Gelled/Dispersed System

The literature does not give a comprehensive description of the microstructure of hydrophobic clays in organic media. The term dispersion has been used to describe the physical appearance of organoclay platelets. Analytical methods to complement this description have been described by Cody and Reichert (1986) who also used SEM images of freeze dried organoclay (2M2Ht) in CCl4 with and without acetone polar activator to illustrate the effects of polar activator interaction. Cody and Reichert (1986) do not provide a detailed account of the microstructure of dispersion. They described organoclay structure simply by : " the structure of the clay platelets is more open, i.e., larger spaces between the platelets, when treated with a polar activator such as acetone." They accounted that the observed open structure was a consequence of activation with a polar activator and that mechanical energy (milling) has the effect of separating agglomerated platelets into smaller stacks.

1.6 Bentone 38 - an Organically Modified Hectorite Clay

Organoclays are used in a wide range of applications for their structuring abilities to modify rheological attributes. Organoclays have high and low temperature stability that is important in aviation, heavy industrial and mining applications particularly in regions of extreme climate conditions. The range of organoclays enables versatility over a wide range of base stocks including paraffinic and naphthenic mineral oils, silicone fluids, polyolefins, esters and biodegradable vegetable stocks.

Organoclays have been used in the cosmetic industry to serve as rheological modifiers, anti-caking agents and for their suspending properties. As with conventional hydrophilic clays, one of their most notable properties is their swelling capability in non-aqueous fluids. This is a characteristic of the smectite clays, particularly noted in hydrophilic applications but now this feature has been applied to the organophilic clays. Their ability to swell and delaminate to form gel networks is the key to the rheological benefits they contribute to all systems they are applied to.

The clay system chosen for study in this project is an organically modified smectite clay called Bentone 38. The chemical name for the clay is dimethyl-dialkyl-ammonium hectorite. The dialkyl groups are thought to be carbon chains (C16-C18 in 70:30 ratio) and are often referred to as di-hardened tallow groups. It is supplied by Rheox Ltd (previously NL Industries) to the customer as dry agglomerated platelet stacks. The literature suggests this clay is designed for use in low to medium polarity systems. In order to deagglomerate and then delaminate individual platelets and thus obtain maximum efficiency from this clay, high shear, good wetting and a polar additive is required (Rheox Ltd Manual). The chemical analysis for Bentone 38 is provided in Appendix 1.1.

1.6.1 Bentone Gelation Process as Recommended by Rheox Ltd.

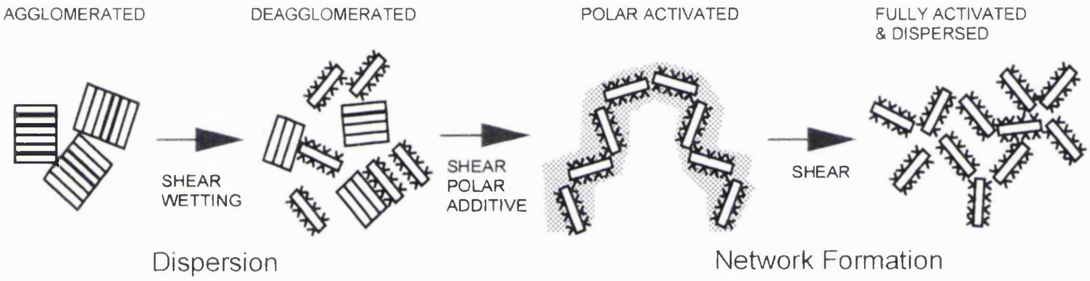


Figure1.10 : Proposed gelation process (Rheox Ltd,1988)

Bentone is supplied as dry agglomerated platelet stacks that must first be wetted out under the influence of shear by a solvent. The solvent penetrates between the platelet layers and forces them apart or deagglomerates the platelets. On addition of a chemical activator or polar additive, still under the influence of shear, the platelets are forced further apart. The result is a thought to be a fully structured gel at this stage. The gelation process illustrated schematically (Figure 1.10).

1.6.2 Incorporation of Organoclay into Process Procedure

Two basic methods for incorporating Bentone 38 into an organic system are recommended in the supplier literature - in-situ or pregel addition. Pre-gel is a preblended mixture of Bentone 38 in a solvent, manufactured by the operating company and therefore will not be regarded in this study. In-situ addition simply refers to addition of Bentone 38 to the system as a dry powder. This method requires a solvent that has good wetting properties and excellent mixing. Bentone 38 is added to organic medium and high shear mixed for 10 minutes to ensure the clay is fully wetted. The polar additive is then added under continued shear for a further 5-10 minutes. The shear device is fairly arbitrary and an effective gel is said to be achievable by using such items as disperser discs, roll mills and homogenisers with emulsifier screens.

The proportion of ingredients recommended is shown in Table 1.3 and only serves as a guideline to the customer.

Ingredient	Procedure	Proportion
Solvent	Mix	87 parts
Bentone Clay	mix (10 min)	10 parts
Polar Additive	mix (5-10 min)	*3 parts

Table 1.3 : Proposed formulation and mixing times (Rheox Ltd -Manufacture of Bentone Pregel)
* Level depends upon additive used

Organoclays are used in a variety of applications as already discussed. One of the common uses of the organoclay is in the cosmetic and personal care industry. Unlike the oil and paint industries, little is known of the microstructure of organoclay for personal care applications. The common solvent carrier in these formulations is usually a volatile silicone fluid. Silicone fluids have been used in personal care formulations for numerous years for their sensory attributes. They are not absorbed through the skin, provide low friction for ease of spreadability without leaving a greasy or sticky residue and repel water which is necessary for many products e.g. sun care products, nail varnishes and antiperspirants.

Silicone fluids are volatile, low viscosity liquids. They are clear, odourless solvents and are used in the cosmetic industries to provide lubricancy and emolliency. Their characteristics include good spreadability, non-greasy and low irritancy. These characteristics are attributed to the fact that volatile silicones have a low surface tension (19-21 dynes/cm @25°C) and low viscosity (<10cs @25°C).

In general, volatile silicone fluids have a low heat of vaporisation with the low molecular tetramer component (D_4) of the molecule evaporating at approximately half the rate of water (at 22°C). This factor enables silicone fluids to replace other volatile solvents in personal care products since silicone fluids do not cool the skin when they evaporate c.f. ethanol.

Silicones are classified by the Cosmetic, Toiletry and Fragrance Assosication (CTFA) as speciality chemicals rather than oils since they are not composed of hydrocarbons c.f. mineral oils.

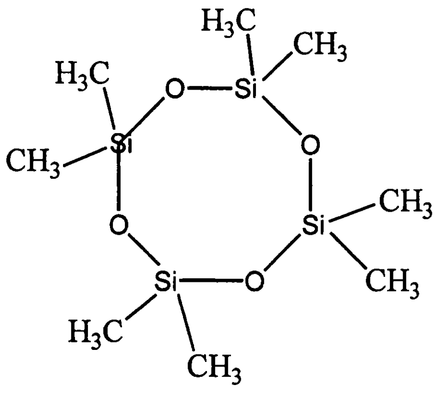


Figure 1.11 (a) : D4 Tetramer
Octamethylcyclotetrasiloxane

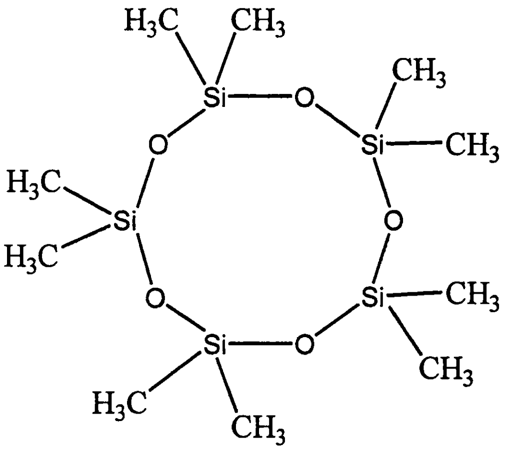


Figure 1.11 (b) : D5 Pentamer
Decamethylcyclopentasiloxane

The chemical name for the silicone fluids used in this study is polydimethylcyclosiloxane but they are often referred to by their generic name of cyclomethicone. As the name suggests, they are cyclic in structure generally having four, five or six siloxy units. The chemical structures of the tetramer and pentamer are shown in Figures 1.11 (a) and (b).

Silicone fluids have one major disadvantage in formulations in that they do not provide the adequate flow rheology required in personal care formulations. Personal care products have to perform under a wide range of conditions. During a product shelf life, flow needs to be restricted to prevent sedimentation however, flow is required when squeezing a product from its container or spreading during application.

Silicone fluids are Newtonian in viscosity, that is, viscosity is independent of shear rate. Low viscosity silicones are selected to provide the correct sensory benefits required for personal care formulations. However, such silicones do not provide adequate suspension or flow properties for product applications. If a higher molecular weight silicone fluid, with a greater viscosity, were exchanged in a formulation, the viscosity for anti-settling of particulates may be perfect but the viscosity would be too high for application making spreadability difficult.

Ideally, a personal care product requires a shear thinning type behaviour starting with a very high viscosity at low shear rate (equivalent to shelf life conditions) to a low viscosity at high shear rates (equivalent to dosing and application of product). It is possible to transfer this preferred viscosity to a low viscosity silicone fluid by incorporating a rheological modifier and this is where the role of the organoclay is important.

By delamination of organoclay platelets, a strong three-dimensional network is generated that yields the required high viscosity at low shear rates. The network breaks down upon the introduction of shear causing the loss of viscosity over shear rate. Organoclays are tailored to meet specific applications and the organic molecule on the surface of the clay is dependent on the bulk liquid phase of the formulation. Trade literature recommends that the most compatible organoclay with silicone fluid should be composed of a quaternary amine. To effectively build this three-dimensional network a third element is said to be required. Polar molecules added in small amounts are believed to be required to intercalate between the platelets of stacked clay and cause swelling of the organic molecule. This enables the clay platelets to separate and form a network. Hydrogen bonding between the plate edges is thought to be responsible for the network rigidity and is said to be achieved by diluting the polar activator by a small degree of water or by utilising the water that exists in trace amounts in general laboratory chemicals (Rheox Ltd). The same principles apply for structuring organoclays in other hydrophobic mediums however, the organic on the clay surface will be selected to complement the bulk continuous phase. This simple ternary formulation is the base for many products for a wide range of applications.

1.7 Summary of Clay Chemistry

Clay minerals have been studied extensively over the last century and a good knowledge of their chemical compositions and lattice structure is known. Techniques such as X-Ray Diffraction and Electron Microscopy have been used extensively to determine the structure of clay particles. Clay minerals exist in their natural form as combinations of tetrahedral and octahedral sheets. The chemical structure of hectorite clays is known to be a 2:1 trioctahedral type smectite. It is the surface chemistry of clays that has been the focus of research over the latter part of the century. Clays in their natural state normally carry a net negative charge that is a result of isomorphous substitution of elements within the crystal lattice. Compensating cations bind to the surface of the clay by means of electrostatic and van der Waals forces.

Understanding of the chemistry of hydrophilic clays is far more advanced than for organically modified hydrophobic clays. In aqueous solution, cation exchange influences the creation of a diffuse electric double layer. Cation-exchange is a major feature of the hydrophilic clay chemistry since it is the cations that influence the properties of the clay. Cation-exchange alters the basal spacing between parallel layers of clays. Basal spacing is dependent on the size of the exchangeable cation.

When hydrophilic clays are contacted with water, water molecules penetrate between adjacent layers and increase the basal spacing of the clay. As the platelets are forced apart, the diffuse double layers begin to repel each other and the clay is seen to 'swell'. When osmotic and hydration forces exceed the attractive forces of the clays the platelets deagglomerate. Upon flocculation three types of particle association may occur: face-to-edge, edge-to-edge and face-to-face. It is the face-to-edge association that results in the structure frequently described as the 'House of cards' structure. This is an electrostatic interaction between the faces and edges of the platelets. This structure has been hypothesised by many scientists although it is only in the early 1990's that SEM and TEM images have claimed to prove the theory.

It is the chemistry of the organo- or hydrophobic clays that is of interest in this project. Surprisingly little is known as to the structure of hydrophobed clays although many theories are postulated. It is known that a wide variety of organic species will surface coat clays. Ammonium ions are of particular interest to this project and it is known than such ions will undergo cation exchange. It is believed that ammonium ions will replace sodium ions stoichiometrically. Little is known about the orientation of such molecules on the surface of clays let alone specifically hectorite clays. Hypotheses regarding simple ammonium ions are given, however, the orientation of quaternary ammonium ions is purely speculative.

It is widely accepted in the field of hydrophobic clays that in order for gel formation to occur the use of a polar additive is required. The role of the polar additive is clear in that it aids gel formation and hence enhances the rheological properties of the system. There are a number of theories as to the way polar additives may react with organoclay species. However, there does not appear to be one defined or proven theory. One such theory suggests that polar additive alone will not create a robust gel and that water is required to create water bridges between platelet edges (Rheox Ltd).

In order to overcome the forces of attraction that hold clay platelets together a certain degree of energy is required, be it mechanical, thermal or chemical. The literature provides limited detailed information as to the type or regime of mechanical shear that is necessary to disperse clay agglomerates. Thermal methods for dispersing clays are even less detailed. Focus is given upon chemical additives that are thought to intercalate the platelets and prise them apart and are deemed as critical to the process.

Viscosity is seen to increase upon clay dispersion however the literature does not detail the microstructure of the system. Viscosity is seen to decrease if too much polar additive is added to the system. It is proposed that when polar additive is added in excess, it blocks the sites on the edges of the platelets thus inhibiting gel formation. The literature does not indicate the stability of gelled systems.

1.8 Aim of Research

This research was a fundamental research into the mechanism of structuring an hydrophobed clay system (Bentone 38) in a silicone fluid medium.

The main objectives of this study were:

- To screen a range of polar activators and determine their effectiveness on swelling Bentone 38.
- To gain an insight as to the affinity of a range of polar activators with clay through electrophoresis.
- To gain an initial understanding of surface force measurements of a model clay in the presence of polar activators to provide information on attractive forces between clay platelets.
- To determine the effects of changing processing parameters has on delamination of clay platelets. This will involve testing a variety of process machines with different shear rate capacities.

- To quantify the shear rate that is required to delaminate clay platelets in silicone fluid.
- To study the effect of temperature on the phase behaviour of Bentone 38 will be investigated. Using this information the effect through processing at elevated temperatures will be evaluated.
- To gain an insight into the effect of temperature and polar activator on swelling behaviour through measurement of basal spacings on a model clay system using X-ray Diffraction.
- To develop a method to visualise and describe the microstructure of the gel network using cryo-SEM.
- To describe an alternative method that optimises gelation of Bentone 38 in a silicone fluid system.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Components of Hydrophobic Formulation

2.1.1 Base Fluid Medium

Two silicone fluids are used in this study. They are supplied by *Dow Corning*®Corporation and are blends of the tetramer and pentamer cyclomethicone. They are referred to by their trade names DC 245 and DC 1465 and some of the typical properties are listed in Table 2.1.

	Dow Corning 245 Fluid	**Dow Corning 1465 fluid**
Composition, %	D_5, 95	D_4, 50 D_5, 50
Colour	Clear	Clear
Specific Gravity, at 25°C	0.95	0.95
Viscosity, cST at 25°C	4.2	3
Refractive Index, at 25°C	1.397	1.395
Surface Tension, at 25°C, dynes/cm	18	17.9
Flash point, closed cup, °C	76	60
Boiling Point, at 760 mm Hg, °C	205	188
Solubility Parameter	7.4	7.4

Table 2.1 : Physical Properties of Silicone Fluids

2.1.2 Structurant/Suspending agent

The organoclay used in this study is known as Bentone 38 and supplied by *Rheox Ltd.* Bentone 38 is used in a wide field of applications including paints, adhesives and cosmetics. It is supplied as a fine, creamy-beige powder of density 1.7g/cm^3@ 20°C. The size of the crystals varies but average dimensions of the dispersed crystals are of the range 0.8 x 0.08 x 0.001 μm (Rheox Ltd, 1988) and are described as being of elongate shape. There are no chemical hazards associated with the chemical and is deemed non-irritant for human use.

Bentone 38 is an organically modified hectorite clay. Hectorite is a member of the smectite group of minerals deriving its name from Hector, Southern California, where it is found naturally in abundance for commercial application. Its chemical composition is $Si_4Mg_{2.67}O_{10}(OH)_2Li_{0.33}Na_{0.33}$ and, as described in Chapter One, is a 2:1 trioctahedral mineral. Hectorite in its natural state is of hydrophilic nature since the outer surfaces of the platelets are balanced with inorganic ions. To yield the organically modified hydrophobic clay Bentone 38, the inorganic species are exchanged for the quaternary ammonium organic cation dimethyldialkyl ammonium chloride. This is sometimes referred to as dimethyl bis (hydrogenated tallow) ammonium chloride or 2M2HT. This has the chemical formula: $(CH_3)_2N\ (C_{18}H_{37})_2Cl$ and is represented in Figure 2.1

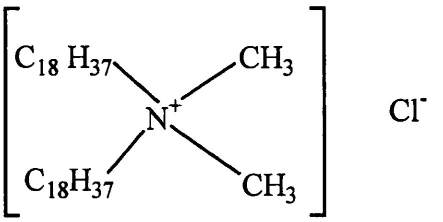


Figure 2.1 : Dimethyldialkyl ammonium chloride

The supplier recommends that Bentone 38 organoclay is designed specifically for application in low to medium polarity systems. The supplier specifies that Bentone 38 is compatible with silicone fluids particularly in the application of personal care products (Rheox Ltd).

2.1.2.1 Commercial Preparation of Bentone 38

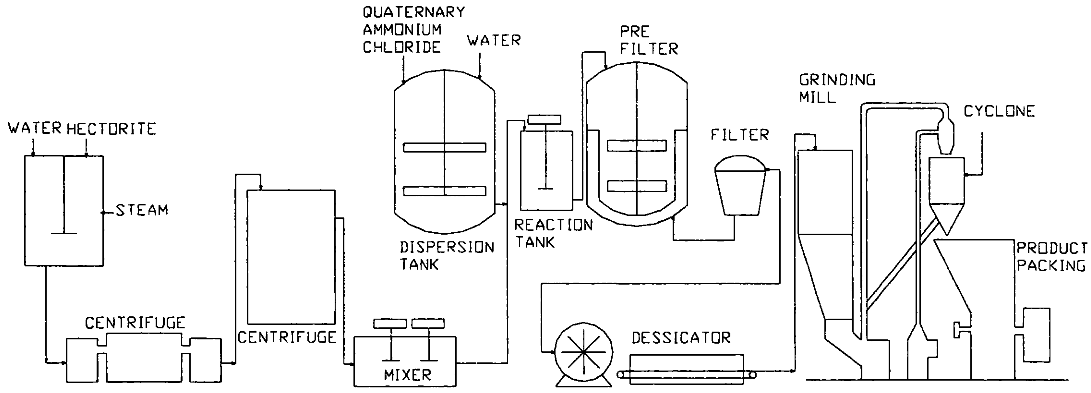


Figure 2.2 : Schematic diagram of Bentone 38 manufacturing process

The preparation of Bentone 38 is accomplished by a cationic exchange process (Rheox Ltd, 1959). The hydrophobic clay complex is produced by first dispersing naturally occurring hectorite in water to produce a dilute slurry. The dilute clay is then subjected to an ion-exchange treatment that causes a replacement of calcium, magnesium and other cations on the surface of the clay particles with sodium ions. Contaminants are removed from the clay slurry prior to converting it to the homionic sodium clay by permitting the contaminants to settle out of the dilute aqueous dispersion of the clay or by super-centrifugation. The dilute clay slurry undergoes an ion-exchange treatment through an ion-exchange column using a fixed bed flushed with a concentrated solution of sodium chloride. The ion-exchange column is filled with a high capacity resin, AMBERLITE IR-120 ™ that is a sulphonate styrene type cation exchanger.

To produce the hydrophobic clay complex, a dilute aqueous dispersion of the ammonium salt (dimethyl-dialkyl C16/18 ammonium compound) is reacted with the dilute slurry of hectorite that has now been converted to the sodium form. A flocculated hydrophobic clay complex forms that is readily separated from the aqueous phase by filtration after which it is washed, dried and ground to produce a fine powder. The process is generic to hydrophobic clay production with variants depending upon the organic compound used for exchange. Figure 2.2 shows a schematic of the process of production of hydrophobic clay.

2.1.3 Polar activator

A range of polar activators were selected for evaluation based on information taken from clay supplier literature (Rheox Ltd and Laporte) that recommends medium to high polarity activators yield the best gel networks. In addition to those recommended by suppliers, a number of polar molecules were selected for their functional group properties and size. The selections were made from a table of polar activators that were ranked on order of efficiency compared to acetone published by the National Lubricating Grease Industry (Appendix 2.1). Finally a non-polar species was also investigated to serve as a control.

2.1.3.1 Propylene Carbonate (polar)

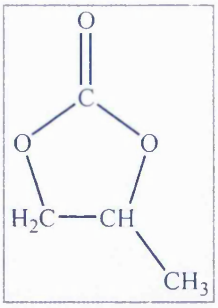


Figure 2.3 : Propylene Carbonate

Propylene Carbonate (Honeywill and Stein Ltd) is the trade name for 4-methyl-1,3-dioxolan-2-one. It is a cyclic molecule (dielectric constant = 67) with formula $C_4H_6O_3$ (molecular weight = 102.088). The structure of propylene carbonate is shown in Figure 2.3. Propylene Carbonate carries a carbonyl functional group that is responsible for its polar properties. Propylene Carbonate is a colourless liquid with a flash point of 123°C.

Under normal conditions propylene carbonate is classified as a stable compound with no unusual reactivity.

Propylene Carbonate was selected as the primary test polar molecule since it is used extensively in applications for structuring Bentone 38 particularly in the field of personal product application.

2.1.3.2 Methanol (polar)

Methanol (Fisher Scientific UK Ltd) Grade Dried distilled Solvent, High Purity Reagent, Batch No 9750030227 (< 0.01% water content). Methanol is a colourless liquid with molecular formula CH_3OH and molecular weight = 32.04. It is the simplest form of the aliphatic alcohol family carrying the OH functional group. It has a dielectric constant of 32.63 and a dipole moment of 1.70 D. It was selected on account of its reference as being an effective polar activator in trade literature.

2.1.3.3 Absolute Ethanol (polar)

Absolute Ethanol (Fisher Scientific UK Ltd) Grade Standard Laboratory Reagent, Batch 9876733108 (water content = < 0.5%). This is the second member of the aliphatic alcohol family with molecular formula C_2H_5OH and molecular weight = 46.07. It has a dielectric constant of 24.3 and a dipole moment of 1.69 D. It is also recommended by trade literature as an effective polar activator for structuring organoclays. It is given the rating of 75% efficient compared to acetone as a polar activator. Absolute ethanol was selected over standard ethanol, an azeotropic mixture of 95% alcohol and 5% water.

2.1.3.4 Propan-2-ol (polar)

Propan-2-ol (Fisher Scientific UK Ltd) Grade Dried Distilled Solvent, Batch 9623978357 (water content = <0.01%). The molecular formula of propan-2-ol is $(CH_3)_2CHOH$ and its molecular weight = 60.10. The dielectric constant of propan-2-ol is 20.1 and it has a dipole moment of 1.68 D. Propan-2-ol is a clear liquid and is the third member of the aliphatic alcohol group.

2.1.3.5 Propanone (polar)

Propanone (J T Baker) Grade Standard Laboratory Reagent, Batch 9530620006. Propanone has a molecular formula $(CH_3)_2CO$ and its molecular weight = 58.08. The dielectric constant of propanone is 20.7. Propanone is the simplest aliphatic ketone and is sometimes referred to by its common name acetone. The polar carbonyl group is responsible for the polarity of this compound. The large dipole moment (2.88 D) indicates that the electrons of the carbonyl group are unequally shared since the mobile π electrons are pulled strongly towards the more electronegative atom (oxygen). Propanone is a colourless liquid that is highly soluble in water. It is frequently cited in the literature as a potential polar activator.

2.1.3.6 Acetophenone (polar)

Acetophenone (Fisher Scientific UK Ltd) Grade Standard Laboratory Reagent, Batch 9767252038. Its molecular formula is $C_6H_5COCH_3$ and has a molecular weight of 120.15. Acetophenone is the common name for 1-phenylethanone, an aromatic ketone. Acetophenone, like all ketones, carries the highly electronegative carbonyl species and it is this species, being a strong deactivating group, which removes electron density from the benzene ring and is responsible for the dipole moment of 3.02 D. Acetophenone is a clear, colourless liquid with a slightly floral odour on account of it being an aromatic ketone. This was selected to compare the effect of a carbonyl species on the degree of swelling in comparison to propylene carbonate.

2.1.3.7 Nitroethane (polar)

Nitroethane (Fisher Scientific UK Ltd) Grade Standard Laboratory Reagent, Batch 9627743346. Nitroethane has a molecular formula $CH_3CH_2NO_2$ and a molecular weight of 75.07. Nitroethane is an oily liquid with a large dipole moment of 3.65 D.

2.1.3.8 Hexane (non-polar/control)

Hexane (J T Baker) Grade Standard Laboratory Reagent, Batch 9515310008. The molecular formula for hexane is $CH_3(CH_2)_4CH_3$ and its molecular weight is 86.18.

Hexane belongs to the alkane group and is composed of atoms linked by covalent bonds. The bonds of alkane molecules are directed in a symmetrical way that cancels out any slight bond polarities between the carbon and hydrogen atoms. As such, alkanes, are non-polar molecules. Hexane is a colourless liquid that is insoluble in water and soluble in hydrocarbons. This aliphatic alkane was selected as a control additive for experimental purposes being non-polar and liquid at room temperature.

2.2 Processing Equipment

2.2.1 Equipment Specifications

Experiments were carried out at 2.0Kg and 30Kg scale for processing the formulation. A description of the rigs used to manufacture the test formulations is given below. Specific details of experimental procedures will be given in the relevant sections following.

2.2.1.1 Silverson L4R Mixers

The standard L4R Mixer (Silverson Machine Ltd) is a bespoke piece of laboratory equipment. It is termed a 'dip-in' mixer since the homogenising head is lowered into a mixing vessel by means of an electrically driven lifting and lowering mechanism. The standard L4R mixer comprises of a shaft that is driven by a motor which turns a four-blade rotor. An emulsifier screen shrouds the rotor and is fixed into position by means of holding screws. A control knob governs the speed of the rotor. As the speed of the rotor is increased liquid is drawn up and forced through the orifices in the emulsifier screen.

The In-line Silverson L4R operates in much the same way as the standard model. The basic rotor and stator components are the same, as is the speed control and driver motor. The key difference is that the in-line L4R Silverson is designed to be built into a rig assembly with the process fluid being positively pumped through the homogenising head with continuous flow rather than relying on the speed of rotation of the rotor to draw the fluid up and through the emulsifier stator. The diagrams in Appendix 4.3

show the basic components of the rotor and stator assemblies of the L4R mixers and the differences between the in-line and dip-in models.

2.2.1.2 2 Kg Mixer Rig

The 2 Kg rig was designed to incorporate an in-line Silverson L4R homogeniser. This ensures that all of the test fluid sees the same quantity of shear regime that is something that cannot be guaranteed when using the dip-in model.

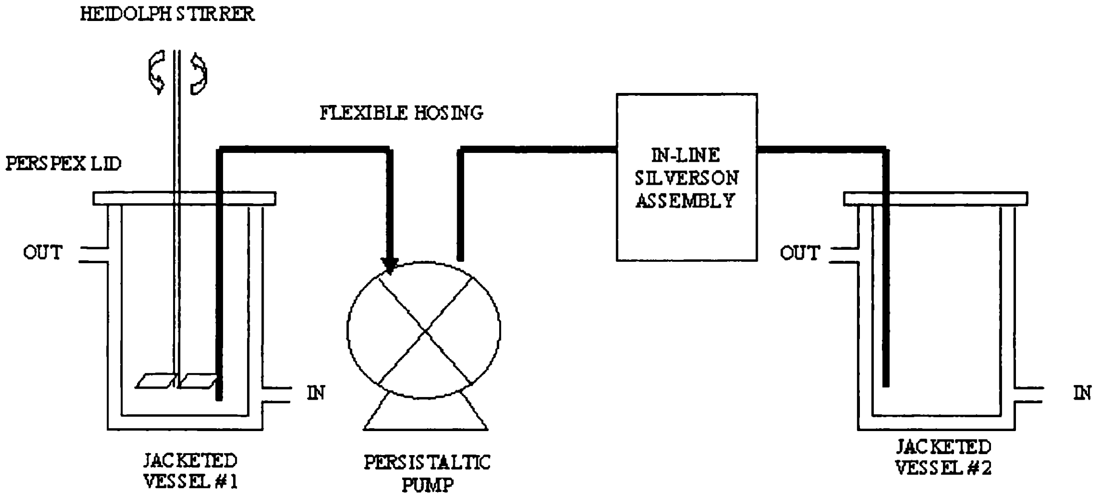


Figure 2.4 : 2kg Laboratory scale In-line Silverson mixing rig

The rig comprised of two jacketed glass vessels (2L). Rubber tubing was connected to the inlets and outlets to allow a constant flow of water through the jackets. In all the experiments performed cold tap water was used however, the design enables connections to a hot water supply e.g. water bath if required. Raw materials were added to vessel A and stirred continuously throughout the process runs with a Heidolph stirrer (Electro, Model RZR5013191) using a paddle impeller (blade, tip speed = 0.1m/s). Perspex lids for each vessel were fabricated and holes drilled in them in order to position stainless steel tubing to the bottom of the vessels. Flexible silicone tubing was connected to the fixed position tubing by means of plastic ties. The mixture was pumped at constant flow rate via a peristaltic pump (Watson Marlowe Ltd. Type MHRF

200) through an in-line Silverson L4R (Silverson Machine Ltd) high shear mixer and into the collection vessel B. The whole procedure was termed as 'one pass' and unidirectional thus to perform the second pass vessels A and B exchanged positions and so on for further passes. Figure 2.4 shows a schematic of the 2 Kg Rig.

2.2.1.3 Pilot Plant 30 Kg Scale Universal Flameproof Mixer

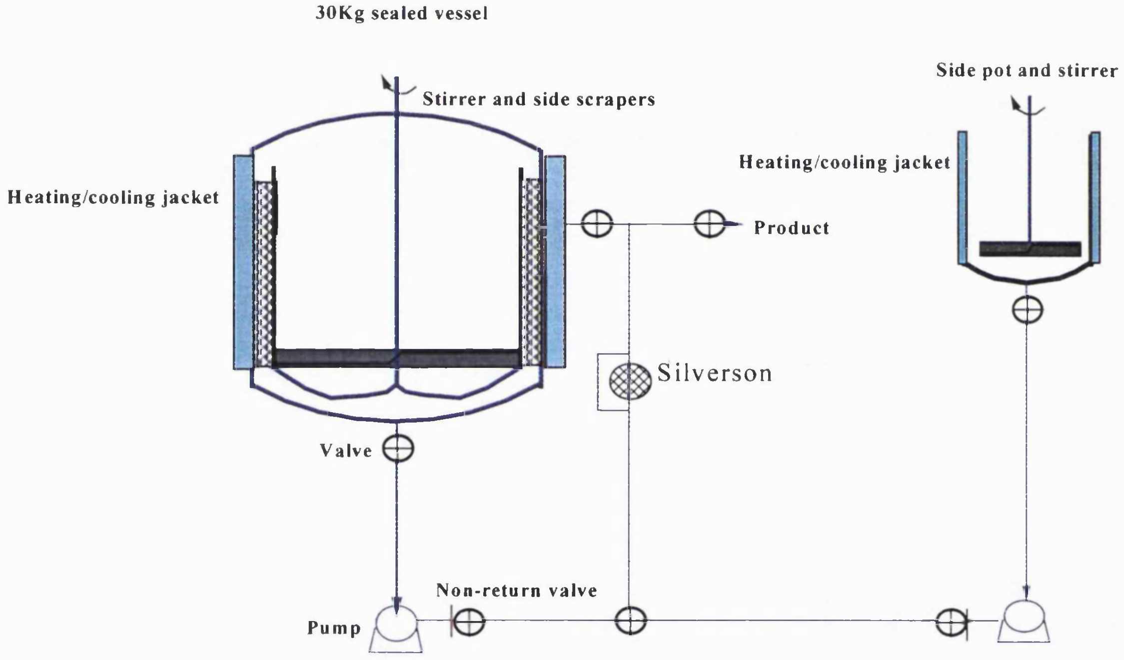


Figure 2.5: 30 kg Pilot plant mixer

The 30Kg Mixer is a custom built piece of equipment specifically designed for processing flammable materials. It is composed of a 30 Kg jacketed sealed vessel with the capability of vacuum and top pressure. It is designed with anchor sweep side scrapers to ensure maximum bulk mixing. The impeller is driven by a variable speed flameproof motor (Brook Hanson, Type SCE24B, 0-90rpm). A variable speed tri-lobe 316L pump (APV Pumps) powered by a fixed speed geared electric motor (BH402-IEC-AE100LBDTP, speed@100 Hz = 140 rpm) feeds product, via a recirculation loop, through a dynamic multi-stage in-line mixer (Silverson, 5000 rpm, double emulsor screens) and back to the vessel and/or discharge. A pressurised water heater (Churchill) controls temperature of the vessel. Figure 2.5 shows a schematic of the layout of the 30 Kg scale Universal Mixer.

2.2.1.4 APV Rannie Flameproof High Pressure Homogenisers

2.2.1.4.1 APV Mini-lab 7.30 VH Homogeniser

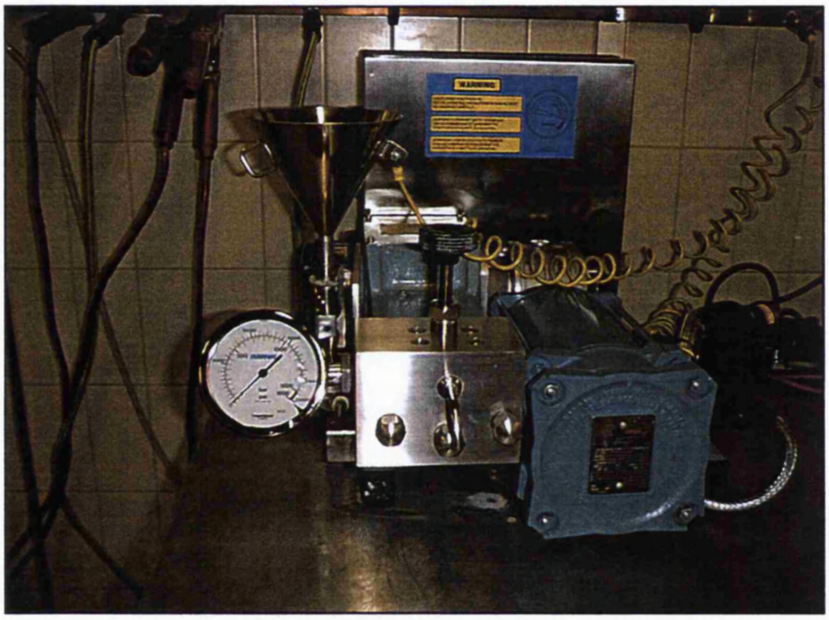


Figure 2.6 : High pressure Mini-lab homogeniser (APV Homogenisers)

A custom built flameproofed version of the standard APV Mini-lab type 7.30 VH homogeniser (APV, Rannie) was used for the ultra high pressure evaluation work that provides extensional shear-flow to products. Product is fed into a funnel and pumped via a small peristaltic pump (Watson Marlow) into the homogenising block. Two pistons force the product through a precision-engineered ceramic valve thus creating extreme pressures. The maximum capacity of the homogeniser is 6.5l/h @ 1500 bar. The Rannie Mini-lab is a laboratory scale piece of equipment as shown in Figure 2.6.

2.2.1.4.2 APV Lab 2000 Homogeniser

The Lab 2000 Homogeniser was also used in high pressure experiments since the APV Mini-lab proved to display mechanical reliability issues. The main difference with the APV Lab 2000 homogeniser is that product is gravity fed via a funnel into the homogenisation chamber and a single piston operates to create the high pressure required to force the fluids through the homogenisation valve. The APV Lab 2000 homogeniser has a maximum operating pressure of 2000 bar and may be used in single or double stage mode. For all experimental purposes, the single stage operation mode was used. A schematic diagram of the machine is given in Figure 2.7.

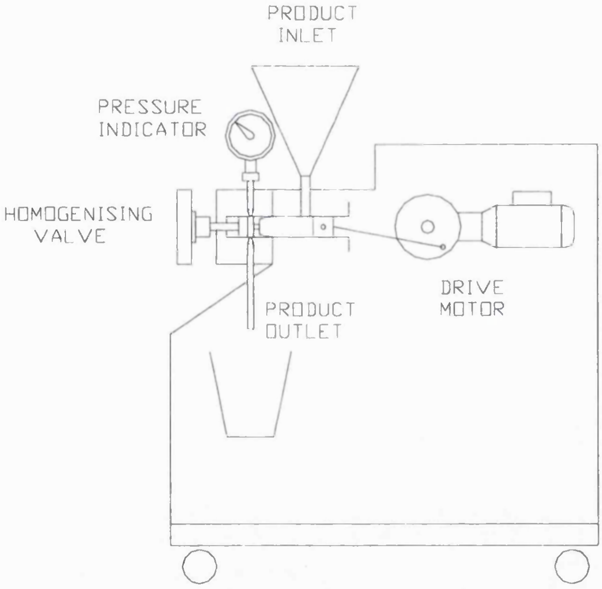


Figure 2.7 : Representation of Rannie Lab 2000 high pressure homogeniser

2.2.2 Formulations

In order to understand the role of an organoclay and the way it functions with respect to external influences such as shear and temperature, it is necessary to use the simplest formulation. Therefore, two formulations were decided upon: a simple binary formulation of organoclay and bulk liquid phase and a ternary system where polar activator is included. The percentage of each ingredient was based on the quantities used for base recipes used in standard cosmetic and personal care formulations and the information supplied by the chemical suppliers. The formulations are given in Table 2.2.

Function	Ingredient	%w/w
Structurant	Bentone 38	6.8
Base Fluid	Silicone fluid 1465	92.2 or 93.3
Polar Activator	e.g. Propylene Carbonate	1 or 0

Table 2.2 : Bentone 38 prototype formulation

2.2.2.1 General Processing Methodology

Specifics for the processing of organoclay is detailed in the experimental sections however, in cases where a pregel was required for specific shear studies it was necessary to pre-manufacture the organoclay base.

2.2.2.2 Manufacture of Pre-gel

Bentone 38 was pre-dispersed in solvent (silicone fluid) using a stirrer (e.g. Heidolph stirrer) for ten minutes at room temperature. The mixture was then sheared through a high shear device (Silverson L4R mixer or Double Screen Silverson, 40,000-60,000 s^{-1}) for ten minutes. Polar activator was then added and the mixture was sheared for a further ten minutes.

2.3 Measurement Techniques

2.3.1 Introduction

To determine the effects of processing hydrophobic clay in non-aqueous systems measurement techniques are essential. The techniques chosen for measurement of organoclay dispersions were selected to endeavour to gain insight into the microstructure and rheological properties of these systems. Four techniques were selected as the standard test methods for experimental purposes: Optical microscopy, Scanning Electron Microscopy, Rheology and Viscosity. A description of each of the techniques follows.

A number of other techniques were evaluated to deem their relevance to the project and a brief description of the technique and why they were not practical is also given.

2.3.2 Microscopy

Microscopy is a useful technique to provide visual evidence of the degree of dispersion. Optical microscopy is a highly efficient technique to be used as an initial screening on particle size reduction and hence dispersion whereas electron microscopy provides detail of the intimate particle relationships and structural arrangements.

2.3.2.1 Optical Microscopy

Optical microscopy is most often used for the examination of species within the range ~ 0.3μm to 150μm. Clay agglomerates are therefore easily visible using an optical microscope. The theoretical lower limit of the optical microscope is approximately 0.2μm but the diffraction halo around the particle gives a gross overestimation of particle size. It is the wavelength of light (~55 nm = green light) and diffraction phenomena which result from the wave nature of light that limit resolution. The limit of resolution (δ) is given by the equation:

$$\delta = \lambda/2n \sin \alpha \qquad \textbf{Equation 2.1}$$

where α is the angular aperture of the objective, λ is the wavelength of the illuminant, n is the refractive index of the immersion medium between the object and objective lens, and $n\sin\alpha$ is the numerical aperture of the objective lens for a given immersion medium. Particles smaller than the limits of resolution appear as diffuse circles and thus image broadening occurs which results in over-sizing. Even particles of size greater than the theoretical lower size limit can undergo distortion and therefore for practical reasons a more realistic lower size is 0.8μm. The most severe limitation of optical microscopy is its small depth of focus (*c.* 10μm x100 magnification and *c.* 1μm at x1000 magnification - total magnification). Focal depth is limited by the objective lens magnification.

Clay agglomerates are within the working range of the compound microscope and therefore an obvious method for imaging the particles. Based on the supplier literature of the particle size of the primary platelets being approximately 1 μm, the technique would not be suitable for accurate particle sizing of individual platelets. It does however provide an indication of particle size. The main advantage of using optical microscopy is that samples may be investigated without the need for dilution compared with other particle size techniques for example, Malvern Mastersizer. A secondary advantage is that particle shape does not have to be considered and compensated for by using model systems. Thirdly, optical microscopy provides immediate information since sample slides may be prepared and fixed throughout an experiment. One of the limitations of the technique is the focal length since Bentone 38 has a wide range of particle sizes it means that only a few particles may be in focus in any field of view however this is easily accounted for. The technique is immediate and quick to perform and therefore ideal for recording information on samples in real time which is an obvious advantage when analysing potentially dynamic systems.

Sample Preparation

- **Dry Bentone 38 powder**

A sample of the powder was shaken from a micro-spatula onto a clean glass slide. A cover slip was placed over the top of the powder and pressed gently with a dissecting needle.

- **Bentone 38 dispersion**

The sample being prepared for analysis was gently agitated. A small droplet of sample was then transferred to the slide by means of a micropipette and a cover slip gently lowered over it. The slide is made semi-permanent by sealing the coverslip with nail varnish.

Analysis of Samples using the Compound Microscope

Samples were analysed on a Compound Microscope (Olympus BH2). This is a differential image contrast microscope (DIC). The objectives used in the study of Bentone 38 and Bentone 38 dispersions were x 20 and x 40 achromats. Images were recorded by capturing the image via a printer that is connected to the microscope. A standard graticule was used to provide a scale for sizing purposes.

2.3.2.2 Scanning Electron Microscopy (SEM)

SEM is a technique that is able to produce good quality three-dimensional images. An electron beam is focused to approximately 4 – 10 nm and scans across the surface of the specimen that is held at an angle to the beam. The electrons interact with the specimen to produce various signals. For example, the low velocity secondary electrons that are emitted are drawn towards a collector grid and fall onto a sensitive detector. It is because the secondary electrons are emitted at low voltage they can be easily deflected to follow curved paths to the detector and because electrons that emerge from out of the line-of-sight may also be collected that they contribute most to the realism of the three-dimensional image.

The magnification range for SEM is 10x to 300,000x. The major advantage of the technique is the depth of field that can be achieved. SEM can give a depth of field 300 – 500 times greater than that available on a light microscope. SEM is frequently used to examine the fine detail of quite large structures because of the depth of focus and has been used to demonstrate surface contours, particle size and orientation. It is for these reasons why SEM was selected as a technique for investigating the microstructure of Bentone 38 dispersions.

2.3.2.3 Standard & Cryo – Scanning Electron Microscopy

Dry sample imaging was carried out using standard Scanning Electron Microscopy (JEOL 840 Scanning Electron Microscope, CIE, Minnesota). This machine operates at 0.2 – 40 kV with an ultimate resolution of 4nm and a magnification range of up to 300,000 x. Standard SEM was also carried out on dry powders using the Scanning Electron Microscope (Measurement Science Unit, URPS).

- **Preparation of Sample for Cryo-SEM**

The cryo-SEM system consists of a chamber for fracturing frozen samples, a coating chamber that uses thermal evaporation to deposit metal films onto the frozen samples and a liquid nitrogen cooled stage that attaches to the existing goniometer. Liquid nitrogen also cools the sample in both the fracturing and coating chambers. Vacuum is maintained at all steps of the process using the SEM's diffusion pump system.

Preparation of cryogenic SEM samples involves three stages: fracturing, sublimation and gold coating. Initially, the standard methodology for aqueous sample analysis was used, however, through investigation it was found that the time and temperature for sublimation is critical. If sublimation is incomplete, silicone fluid 'swamps' the image and definition of structure is impaired. Conversely, if the system is over sublimed, the structure is visible but the network collapses. Optimisation of the cryo-SEM technique for Bentone 38 clay samples in a silicone fluid environment was developed at the CIE, Minnesota (Carew et al, 1998).

A sample was transferred to a rivet and impact frozen on a copper block using liquid nitrogen (-196°C, Reichert-Jung Leica KF80). The rivet was transferred to the cryo preparation chamber (CT 1500) to be fractured before being transferred to the sample stage in the sample chamber to be etched. The sample was then returned to the preparation chamber to be coated with gold and finally transferred to the sample chamber for imaging.

2.3.3 Rheology

The term rheology means the study of the deformation and flow of matter. The term flow is usually a term that is associated with the motion of liquids however it may also apply to solids and gases.

The main characteristic of a clay dispersion is that it is a suspension of flocculated particles and therefore the main rheological concern is that the solid matter wants to settle to the bottom by forcing the liquid to move out of its way. The rheological properties of dispersed systems depend upon the following factors: viscosity of the fluid medium, concentration of the suspended matter, the size and shape of the suspended particles and the forces of interaction that occur between the particles.

The term viscosity is described as follows by Barnes et al (1989):

(1) Qualitatively, the property of a material to resist deformation increasingly with increasing rate of deformation.
(2) Quantitatively, a measure of this property, defined as the shear stress divided by the rate of shear in steady simple shear flow. Often used synonymously with the apparent viscosity. Pa.s.

When particles in clay suspensions interact or flocculate, attractive forces prevail between the platelets and the solvent is trapped between the particles. As a consequence the apparent viscosity of the suspension will be higher than might be predicted. A matrix or structured network is formed when there is a net attraction between particles and this is only achieved when there is a sufficient concentration of particles in the formulation. The network that forms develops a critical yield stress - *the stress corresponding to the transition from elastic to plastic deformation* or, in simplistic terms, the point at which a product flows. Beyond this critical yield stress the structured network is destroyed and apparent viscosity decreases. The magnitude of the yield stress is related to the forces required to break the individual links and the number of links between particles.

Rheological profiling has proved to be an extremely useful tool in determining the structuring effects for many different types of systems e.g. emulsions. Evaluation of suspensions is somewhat more difficult since the stability of a suspension is a critical feature for this technique to be suitable. Rheology has been widely recommended in the open literature for measuring the effects of polar activators in the formulation of clay suspensions and therefore it was chosen as one of the techniques to be evaluated. The experiments performed showed that the suspensions investigated were too unstable to be able to draw any significant conclusions regarding microstructure. An attempt to explain why rheology was not the optimum technique is given in each relevant section and includes alternative considerations for the technique.

A number of factors need to be considered when using rheology as a technique. Difficulties can arise in smooth walled geometries because placing a structured liquid next to the wall changes the local microstructure. For a simple suspension e.g. of smooth spherical particles, the spatial concentration of particles deep in the bulk of the sample well away from the wall is random. However, in the proximity of the wall, the particle concentration is zero. The concentration rises rapidly from the wall to the point where the bulk concentration is encountered (usually about five particle diameters). The result of the differences in concentration of the sample next to the wall and the bulk sample is that the zero concentration zone acts as an effective lubricating layer. This phenomenon is known as wall depletion or commonly termed 'slip'. The effect is very particle size dependent and, in a clay system, this refers to the size of the flocculated particles. Flocculated particles are shear rate dependent. This means that flocs are biggest at low shear rate and therefore for flocculated systems as in clay suspensions, the problem of wall depletion is often encountered i.e. wall slip is a low shear rate phenomena. Roughened geometries or profiled wall are used to eliminate the wall depletion or slip effects e.g. roughened cone or a wire basket.

Evaporation is also a critical effect, particularly in cone and plate geometries where drying at the edge of the samples leads to large errors in the measured torque, given that the effect is at the greatest distance from the centre. This is overcome by using a solvent trap or containing the sample in a sealed environment. The clay suspensions investigated in this work project would be susceptible to solvent evaporation since silicone fluid is a volatile substance. For the low shear rate experiments, where experimental duration is significant a seal was used to minimise the effect of evaporation.

The most significant effect that is encountered with the clay suspensions is the effect of sedimentation. When the sample is sheared, the continuous phase viscosity is greatly reduced and its ability to keep samples in suspension can be significantly effected. The only answer to completely overcome this problem is to slowly circulate the suspension, pumping it out of the bottom of the sample chamber and returning it to the top. The flow rate needs to be adjusted so that the average viscosity of the liquid down the viscometer gap is small compared with the velocity of the wall. This equipment was not available in the laboratory at the time these experiments were carried out however it would be worth considering for future work.

An alternative method is to use concentric cylinders. Provided the gap between the two concentric cylinders is small enough and the cylinders are in relative rotation, the test liquid enclosed in the gap experiences an almost constant shear rate. This is the most suitable alternative to the circulation geometry. The concentric cylinder geometry was not available for the Carri-med Rheometer although they are commercially available.

The other factor that should be considered is the effect of particle size or more pertinent to clay suspensions, is floc size. Large solid particles can become jammed in narrow parts of certain geometries e.g. cone and plate, however, the cone truncation helps reduce this effect. In addition, if the gap is not around five to ten times larger than the largest particle, then the correct viscosity of the material may not be being measured since the particle spatial distribution is being altered by the wall.

To conclude, the formation of flocs traps part of the continuous phase, which leads to a bigger effective phase volume than that of the primary particles. This gives an additional increase in the apparent viscosity over and above that expected from phase volume of the individual particles. When clay floc suspensions are sheared, the flocs rotate, possibly deform and, if the applied stress is high enough, begin to break down to the primary particles.

As such flocculated clay suspensions take time to break down and rebuild and thixotropic behaviour is therefore usually associated with these species. The driving force to rebuild the floc is Brownian motion and since this increases with decrease in particle size, the rate of thixotropic change is a function of particle size. Thus it would be expected that systems with larger particle suspensions to recover their viscosity at a slower rate than systems of small particles. Similarly, large particle suspensions will break down faster under shearing.

Flocculated systems usually have very high viscosities at low shear rate and are very shear thinning which often give the impression of what is frequently termed an apparent yield stress i.e. the point at which there is a dramatic drop in the sample's viscosity as the shear rate is increased. Clay flocculated suspensions display this phenomenon.

The rheology measurements made in this study are simply viscometry measurements. Viscometry is the science of the measurement of viscosity. Such viscometric measurements generally have to do with applying either a force F or a velocity V at a surface in contact with a constrained test liquid or suspension. The response of this liquid to either the velocity or the force is measured at that surface or at some other surface which is also in contact with the liquid. The aim of such viscometry is then to convert the applied force to a shear stress and to convert the velocity to a shear rate. This is done using geometric constants and evaluated at a standard reference point such as the outer edge of the cone and plate, the inner cylinder etc. The calculated shear stress and /or shear rate can be plotted as a function of one another, or else the shear stress can be divided by the shear rate to give the viscosity. Modern rheometers have the computational facilities to enable these calculations to be made automatically and record data simultaneously.

The Carri-med Rheometer was used to take the viscometric measurements of the clay flocculations and gels in this study.

The rheometer is also a tool for measuring the viscoelastic properties of samples. In all structured liquids there is a natural rest conditon of the microstructure that represents a minimum energy state. When these liquids are deformed, thermodynamic forces operate to restore this rest state. This is likened to a stretched spring which will always try to return to its unextended length. The movement from the rest state represents storage of energy. This energy is the origin of elasticity in a liquid. The rest state for a suspension is the spatially random distribution of particles at rest.

Initially, the restoring force increases linearly with the distance that deformation takes the material from its rest state, but eventually non-linearities will be encountered. The rate of increase of the force with deformation then diminishes until at very large deformations a steady state situation arises and the elastic force becomes constant. By the time these large elastic forces are evident, the microstructure of the sample has changed radically. Along side these elastic forces are the ever-present viscous forces due to dissipation so that together these produce viscoelastic effects.

Most concentrated structured liquids show strong viscoelastic effects at small deformations and their measurement is a very useful probe of the microstructure. There are a number of ways of measuring linear viscoelastic response. One of the simplest is the sudden application of a constant stress to the liquid being tested and the monitoring of the resultant strain thereafter. This is known as creep testing. Another frequently used method is oscillatory testing, i.e. applying and oscillating stress or strain as an input to the liquid and monitoring the resulting strain or stress output.

The major disadvantage of the creep test is the duration of the test – as the name suggests, it is a time consuming methodology that is inappropriate for clay suspensions that are readily prone to rapid sedimentation. The oscillatory test measures over a range of fequencies. Short times correspond to high frequencies and long times relate to low frequencies. Short time and hence high frequency is dominated by elastic response and likewise the viscous response that dominates at long times in creep tests, are most important at low frequencies. Since the region of most interest for clay suspensions requires low frequencies, the duration of the experiment is a limiting factor when considering this technique. The conclusion was that only the viscometric measurements would be practical for suspensions that are prone to rapid sedimentation.

2.3.3.1 Carri-med CSL Rheometer

The Rheometer used for all the experiments performed was the Carri-Med CSL Rheometer (TA Instruments). This instrument provides controlled stress experiments that is used to characterise products and can provide a wide range of information such as flow behaviour, structure and dispersion stability. The Carri-Med is mechanically simple and computer controlled. A non-contact motor applies torque (stress) to a sample through a measuring system supported on an air bearing. Measurement of the resultant displacement (strain or strain rate) is gathered and analysed using specially designed software packages for flow, creep or oscillation. The advantage of using the Carri-Med CSL Rheometer is that it can measure a very broad range of shear stresses in a single experiment. The most suitable geometry for experimental purposes is the vane and basket. This geometry comprises a vane (four blades set at 90^0) and basket (a close fitting wire mesh cylinder inside the outer containing cylinder). The vane and basket is used since, like roughened cone and plate geometries, it eliminates wall effects and prevents slip. The cylinder block is maintained at a constant temperature (25^oC) by using a peltier heating block and a Haake water bath. The cylinder is charged with the suspension and covered with a small perspex disc to reduce evaporation of solvent. Other geometries also used included a profiled cone and plate arrangement. A 4^o roughened cone was used for these experiments. The sample was pipetted onto the plate and the cone lowered into place. It is conventional to use a solvent trap to eleiminate evaporation of product by maintaining a solvent rich environment, however since the experimental duration was ten minutes for each sample a solvent trap was not deemed necessary. A cover was placed over the sample for each run. Figure 2.8 shows a digital image of the Carri-med CSL Rheometer used for experimental purposes.

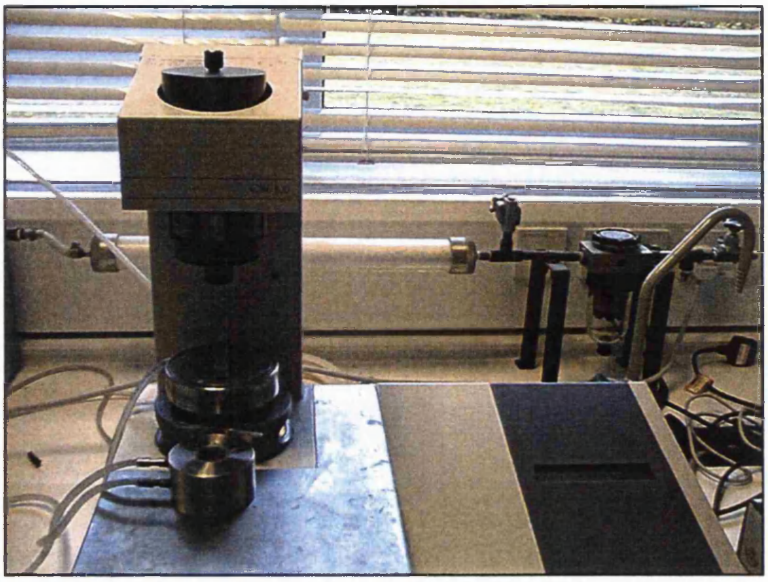


Figure 2.8 : Digital image of Carri-med CSL Rheometer

2.3.3.2 Experimental Procedure

The Carri-Med was run in the stepped ramp (equilibrium) flow mode. Shear rate was monitored under a range of applied stress until equilibrium was attained. Since this is a time dependent factor an overriding time limit was set in the programme. An example of the parameters selected for each experiment can be found in Appendix 2.2. Since apparent viscosity is measured by the ratio of shear stress to shear rate, the log viscosity was plotted against log shear rate to give the viscosity profile of the sample. A typical flow curve is shown in Figure 2.9.

The first point to note is the plateau at low shear rates. This is known as the first Newtonian plateau (the value of which is known as the zero shear viscosity). The viscosity is constant in this region because no structure is being destroyed. The second feature to note is the sharp decrease in viscosity (also known as the Power Law region) as the shear rate is increased. This is the region where structure is being destroyed. Finally when the structure has been destroyed completely, the viscosity becomes constant and this region is termed the second Newtonian plateau. All the experiments were run at very low shear rates (10^{-3} - 10^{-1} s^{-1}) since this is the region that provides information on suspensions of particles.

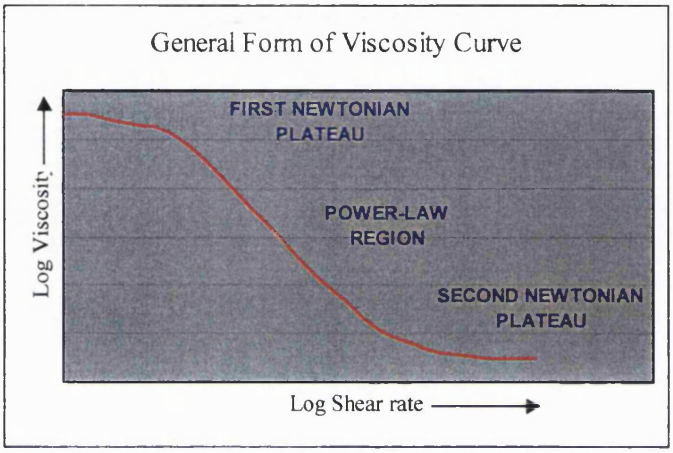


Figure 2.9 : Typical rheological flow curve

The other measurement that can be performed using a Carri-med rheometer is to determine the mechanical response of stress or strain to provide information of the viscoelastic phenomena of structured liquids. This method is a useful tool for understanding thixotropic materials. Thixotropy was defined by Pryce-Jones (1934) as "an increase in viscosity in the state of rest and a decrease in viscosity when submitted to a constant shearing stress" however a more recent definition is provided by Barnes et al (1989) as "a decrease in the apparent viscosity under constant shear stress or shear rate, followed by a gradual recovery when the stress or shear rate is removed. The effect is time dependent"

In theory, Bentone 38 gels can show thixotropy, because thixotropy reflects the finite time taken to move from one state of microstructure to another and back again. The changes in microstructure are brought about by break-down due to flow stresses, build-up due to in-flow collisions and Brownian motion. The timescale for such changes range from seconds to hours, with rebuilding taking much longer than breakdown.

When a thixotropic material is placed in a viscometer (rheometer) and a constant shear rate is applied, the measured viscosity will decrease with time but it will eventually steady out to a constant value. If the shear rate is removed and the material is allowed to rest for a long period and then the shear rate is then reapplied, the measured viscosity will be initially higher but it will then again decrease and end up at the same value as the original cycle after long term shearing. There are a number of reasons why Bentone 38 in silicone fluids are difficult to measure using this technique. This measurement is particularly sensitive to artefacts for example, drying, sedimentation or separation. The samples of Bentone 38 and silicone fluid, in general took the form of liquids that were highly sensitive to sedimentation over short periods of time. Secondly, the silicone fluid is a volatile silicone fluid and would evaporate over the duration of the experiment (even if a solvent trap was used). Another factor of this measurement is that it is highly sensitive to the history of the sample for example, the shear exerted by loading the sample onto the instrument has an effect on the viscosity. One way to eliminate this is to allow a long period for the sample to rest and reach equilibrium (again sedimentation and volatility would have an effect on this measurement). The other major factor that effects the rheological history of a sample is when the gap is set during experimental set up. Here the geometry is rammed up and down to set a known gap. The forces that are exerted through the gap setting clearly would give each sample a rheological history. To complicate matters further when the experiment is ready to be run, the rheometer automatically rams the geometry down to the sample at the pre-determined gap setting, that applyies an unknown downward force on the sample. Finally, wall slippage where shear stress or shear rate is not constant spatially also causes artefacts involved in measuring thixotropy. This can occur as a result of sedimentation with a silicone layer causing slippage or from the presence of large agglomerates or flocs of material.

To summarise, despite this being a very highly informative rheological technique, the practicalities of practising this technique with Bentone 38 systems pose too many artefacts that can cause anomalies in the results obtained. Consequently a compromise technique was established. A short time span experiment known as a loop test was devised. This was where shear stress was increased linearly to a maximum value (5 Pa) and the viscosity of the product was recorded. This was a quick, qualitative procedure but enabled samples to be evaluated before separation of particulate matter had been completed. At best, this procedure could display trend behaviour in a comparative study.

2.3.4 Brookfield Viscometer

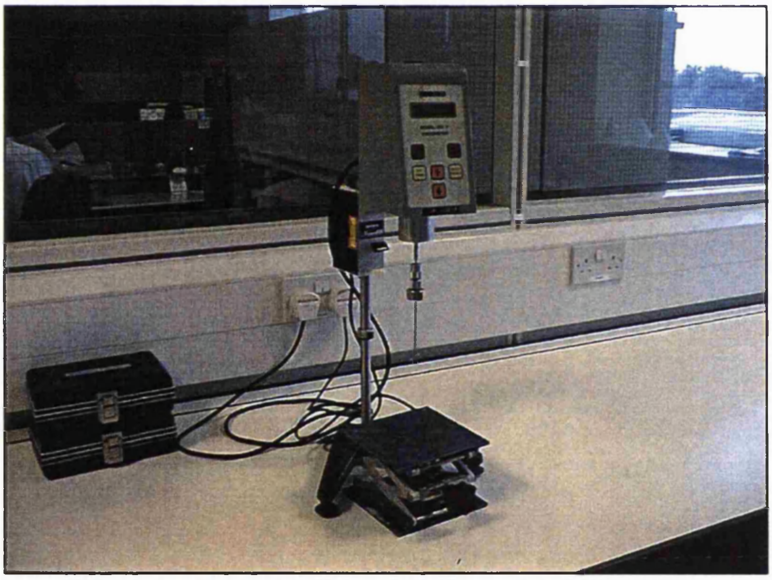


Figure 2.10 : Brookfield Viscometer

The Brookfield DV-1+ viscometer measures fluid viscosity at given shear rates. Viscosity is the measure of a fluid's resistance to flow. The principle of the technique is to drive a spindle that is immersed in the test fluid through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The DV-1+ Viscometer is able to measure over a number of ranges since, for a given spring deflection, the actual viscosity is proportional to the spindle speed and is related to the size and shape of spindle. For a material of given viscosity, the resistance will be greater as the spindle size and/or rotational speed increase. The minimum viscosity range is obtained by using the largest spindle at highest speed and the maximum range by using the smallest spindle at the slowest speed.

The viscometer is fitted onto the Brookfield Helipath stand. A spindle in the form of an inverted T is fitted to the viscometer. As the spindle is rotated, the Helipath stand lowers it through the test material. The resulting path traced by the spindle crosspiece is that of a helix. These two factors ensure the crosspiece is constantly encountering new material thus the rotor always measures material that has an undisturbed structure. The torque required to rotate the spindle is registered, converted to centipoise (cP) and the reading is displayed on a digital panel. Figure 2.10 shows a digital image of a Brookfield Viscometer.

2.4 Review of Cited Techniques

2.4.1 Introduction

The techniques cited in the literature (Cody and Reichert, 1986), infra-red spectroscopy and X-ray diffraction were investigated as potential techniques for determining the properties of organoclays.

2.4.2 Infra-red Spectroscopy

Schaeffer et al (1971) first used infra-red spectroscopy to account for evidence of dispersion of clay agglomerates. They monitored the infra-red vibrational couplings between silicate molecules in adjacent platelets. Si-O-Si stretching motions absorb at ~1040cm^{-1} in the infra-red spectrum. They claimed that when the Si-O-Si motion in one platelet interacts with a similar Si-O-Si motion in an adjacent platelet via a resonance mechanism i.e. coupling, a broad band of coupled frequencies leads to a dramatic decrease in the 1040cm^{-1} band width. When the distance between platelets increases upon dispersion, the Si-O-Si coupling diminished and the bandwidth was observed to narrow. It was concluded that this was evidence that the platelets were increasingly dispersed in the system.

Repeating this technique with a Bentone 38/Silicone Fluid dispersion an attempt was made to repeat this test. Unfortunately, the silicone fluid obliterates the said 1040cm^{-1} peak completely and thus this could not be used as a standard technique for evaluating dispersions of the standard formulation. The spectra for Bentone 38 clay and Bentone 38/silicone fluid are given in Appendix 2.3.

2.4.3 X-ray Diffraction (XRD)

XRD is one of the principle tools for the analysis of clay minerals and is used to investigate structural composition at the molecular level. The most common application is to determine the positions of atoms in crystals. If these atoms are chemically bonded to each other, the technique yields the positions of the atoms in a molecule. Diffraction patterns are run at high angle mode to measure characteristic atomic distances. Over the years a catalogue of mineral diffraction patterns has been established enabling quick identification of clays.

The mode of low angle XRD provides data on interplanar or basal spacings and this is where it provides practical data with respect of clay minerals. Cody and Reichert (1986) used XRD to measure the basal spacings of organoclays. They measured the basal spacing for an organoclay (dimethyldihydrogenated tallow ammonium bentonite) in mineral oil to have a typical basal spacing of 27Å. The basal spacing increased with the addition of a polar activator (2,5 hexanedione) to 37.6Å and similar spacings are observed for acetone activated systems. They also state that a full dispersion is achieved when the reference peak is no longer observed.

The technique was deemed as an extremely informative tool for determining the effect of polar molecules on swelling properties of organoclays and therefore was investigated as a potential technique. The instrument used by Cody and Reichert was a powder diffractometer. It was not possible to have the local equipment on site set up for regular testing of powder samples therefore a specific programme of work was performed at Oxford University in collaboration with the Theoretical and Physical Chemistry Laboratory to investigate swelling of basal spacings. The X-ray diffractometer at Oxford University is a single crystal diffractometer which meant that Bentone 38 could not be evaluated. Vermiculite clay coated with the quaternary ammonium was used to model Bentone 38. Details of the work will be found in Chapter 5.

2.4.4 Particle Sizing

Particle Sizing was initially thought to be the obvious measurement technique for measuring dispersion. There are numerous techniques commercially available that range from simple seiving techniques to laser scattering. A number of techniques were considered e.g. Malvern Mastersizer and Lasentec however it was decided that optical measurements would be most practical for organoclay dispersions. The reason for this decision was due to the fact that the shape of particles influences size characterisation greatly. Techniques for particle sizing are generally based around mono-dispersed particles in dispersions that are highly regular in shape against which physical models are tested. Since organoclay platelets are far from being spherical, in fact completely the opposite having thin, sheet like dimensions, it was concluded that the conventional methods were not ideal for determining accurate particle proportions.

In addition to this, the size of primary particles is said to be nominally sub-micron meaning that they are right on the lower limits of detection in conventional laboratory technologies.

2.4.4.1 Lasentec

The Lasentec is a particle size method known as Stream Scanning and measures individual particles in real time. The Lasentec measures the particle size distribution of particles or more precisely, the chord length of particles in suspension by employing a scanning infra-red laser beam to illuminate individual particles in its path. A detector picks up back-scattered light pulses and it is the time that the particle is in the beam that determines the chord length of the particle. The measurement of chord length provides information on distribution of particle geometry and particle count. One advantage of this technique is that the focal point is approximately 1mm in front of the window of the probe and since it is inserted directly into the sample suspensions of reasonably high concentration may be evaluated. The size range varies from 0.8 μm - ~250 μm.

Although shape, per se, is not a limiting factor to this technique, the fact that chord lengths are measured randomly across any two outer points of the particle or agglomerate means that absolute particle size cannot be measured. It is therefore necessary to analyse trends in data rather than size absolute. This technique was not progressed in account of the lower size range of Bentone 38 particles being below the lower limits of the Lasentec equipment.

2.5 Summary

Firstly, a description of the three components required to formulate a hydrophobic gel was given. This comprised three key elements : Bentone 38, a silicone fluid and a range of polar activators. A brief description of the processing equipment that was to be evaluated was then provided. A range of processing equipment was selected to cover a wide shear rate range. To analyse the samples, a number of analytical techniques were evaluated and four techniques were selected. This included optical microscopy, Scanning electron microscopy, rheometry and viscosity measurements. A number of additional techniques were also reviewed and an explanation for why they were not selected as standard techniques was provided. Specific methods and procedures that were not standard to this project are explained in more detail where relevant in subsequent chapters.

CHAPTER THREE

THE EFFECT OF CHEMICAL ADDITIVES

3.1 Sedimentation Studies

The first stage of experimental work towards development of the mechanism for effectively dispersing Bentone 38 platelets in non-aqueous fluids was to determine the effect of chemical additives. The manufacturers' literature suggests that the role of the polar activator is effective in the gelling stage of the mechanism. The following experiments were designed to determine whether polar activators contribute also to the dispersion stage of the complete gel formation mechanism.

It is stated in the literature that in order for dispersion to occur, it is essential for the solvent or liquid phase to have a degree of polarity (Jones, 1983). The initial experiment was designed to determine whether a non- polar solvent (silicone fluid, DC1465) would intercalate the platelets. The solvent was also dosed with polar ingredients that were recommended in supplier literature to determine whether this statement was correct. In order to minimise any other forces that may be attributed to dispersion, the clay was subjected to low shear mixing (hand shaken) initially.

The experiments were then repeated. This time a degree of shear was introduced to the series to determine whether a significant difference on Flocculation Ratio would be achieved with mechanical energy. The shear rate is comparable to, or greater than, experiments described in the literature, which lay claims to optimal dispersion being achieved by these methods (Materson and Hahn, 1982).

Flocculation Ratio was measured by dividing the level of sediment after a period of standing by the initial level of clay measured. Small glass universal vials were used for all measurements and the experiments were repeated in triplicate and the means calculated.

3.2 Experimental

3.2.1 Determination of Flocculation Ratio of Bentone 38 in Liquid Media

3.2.1.1 Test One

A small amount of Bentone 38 (0.5g) was weighed accurately into glass vials. The vial was tapped lightly to level the powder and the height recorded. Initially, a quantity of the test liquid (Silicone Fluid 1465, Water, Ethanol or Propylene Carbonate) was added (1ml up to13 ml) to each series of vials. The vials were then shaken by hand (1 min) and left to stand (1 h). The resulting sediment level was measured.

3.2.1.2 Test Two

The experiment was then repeated using mixed solvent/polar additive systems. Solvent (silicone fluid 1465) was added to Bentone 38 (0.5g) at varying levels (5 ml, 6 ml, 10 ml and 13 ml). To each set, a polar activator (propylene carbonate, ethanol) was added at 1%, 2%, 5%, 10% and 20% w/w. The samples were hand shaken (1 min) and allowed to settle (1 h) before recording the level of the sediment.

3.2.1.3 Test Three

Finally, to determine the effect of shear, Bentone 38 (5g) was weighed into a stainless steel beaker. Silicone fluid 1465 (100ml) and polar activator was added (Propylene carbonate) (1%, 2%, 5%, 10% and 20% w/w) to the beaker and mixed using a Silverson L4R mixer (max. speed 9900 rpm, 2 min, emulsifier screen, shear rate 60,000s^{-1}). An aliquot of each test mixture was measured into a small glass vial and allowed to settle for 2 hours. The Flocculation Ratio was then calculated.

3.2.2 Sedimentation Studies of Bentone 38 Suspensions

To gain a better understanding and to rank the effectiveness of polar activators a more comprehensive and structured experimental plan was necessary. The previous set of experiments gave only an insight into the effectiveness of polar mediums using very simplistic techniques and limited control over external variables. It was therefore necessary to design an experiment using a more controlled environment where shear rate was constant, temperature was regulated and sedimentation time was of a duration sufficiently long enough to be satisfied that a stable state had been reached. In addition, the sample vessels used were measuring cylinders allowing for more accurate measurement of clay sediment. For this, a 2-Kg rig was specifically designed (detailed in Chapter Two) to enable constant mixing and controlled temperature.

In addition to the experimental detail, a wider range of polar activators was investigated. These were selected from a list supplied by the NLGI (Appendix 2.1). The list details a range of polar activators and compares their effectiveness as a polar activator using acetone as the benchmark. Other polar activators were selected for their functional group, which is postulated to have an effect on dispersion. Finally two non-polar additives were selected as controls.

Each set of experiments was repeated three times to ensure validity of results. The experiments included a series of measurement techniques in order to qualify observations noted.

3.2.3 Manufacture of Test Suspension

Bentone 38 (67g), Silicone Fluid 1465 (923g) and Test Additive* (10g) were weighed into the glass vessel of a custom-built laboratory rig (In-Line Silverson L4R Mixer Rig) detailed in Chapter Two. Cold tap water (~22°C) was passed through the jackets of the mixing vessel and receiving vessel to maintain the mixture at effectively constant temperature and to cool the mixture post shearing. The mixture was stirred using a Heidolph stirrer (Paddle Impeller, 5 minutes) to wet out the powder and disperse any large agglomerates. The mixture was fed at constant flow rate through an In-line homogeniser (9900rpm, emulsifier screen, shear rate 60,000 s^{-1}) via a peristaltic pump (Watson Marlow, max speed). A total of five passes through the in-line homogeniser completed the process.

*** Test Additives**

- Propylene Carbonate
- Absolute Ethanol
- Methanol
- Propan-2-ol
- Propanone
- Acetophenone
- Nitroethane
- Hexane

3.2.4 Sedimentation Analysis

Sedimentation was measured immediately after the test suspension had been manufactured. An aliquot (24.0g) of suspension was weighed into a 50cm^3 measuring cylinder and sealed to prevent evaporation with a stopper. Sediment height was recorded at regular intervals over a period of one hour. The samples were then stored at constant temperature (28°C) for the period of one month. Sediment height was measured periodically over the duration, daily for the first week and weekly for remaining three weeks.

3.2.5 Measurement Techniques

To complement the measurement of sedimentation, the following analyses were performed on the samples immediately after processing :

- A sample was taken for direct observation of particle images using an Olympus BH2 Microscope. All samples analysed were investigated using DIC at x200 magnification.

- Viscosity was measured using the Brookfield Helipath Viscometer. The TA spindle was used for all samples and the Helipath set at 10 rpm.

- The samples were also run on the Carri-Med CSR Rheometer (TA Instruments). The geometry used was the cone and plate. A roughened cone was chosen to minimise the slip incurred when silicone fluid is used in the formulation. A flow curve was generated for each sample using TA software, the up curve and down curve took ten minutes to ramp between 0.1 and 5 Pa. Ten minutes was determined to be the optimum time to measure these samples on account of the high potential of sedimentation. It was not possible to obtain results for samples that sedimented too rapidly due to slippage.

3.3 Results

3.3.1 Flocculation Ratio at Low Shear Mixing (Polar activator = neat)

Figure 3.1 : Graph to show the effect of solvent volume (ml) on the flocculation ratio of Bentone 38 (0.5g). Low shear mixing = hand shaken (1 minute), n=3

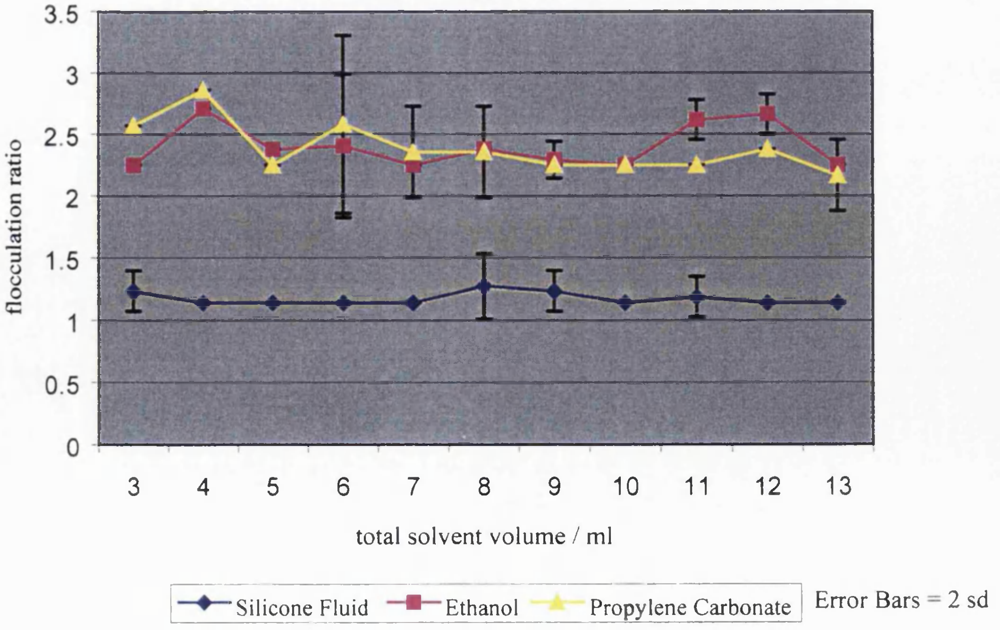


Figure 3.1 shows the mean Flocculation Ratios of Bentone 38 in neat solvent systems over a range of fluid volumes for silicone fluid 1465, propylene carbonate and ethanol. Water has been omitted from this graph since the Bentone 38 flocculated immediately on account of its highly hydrophobic nature and sediment height was not measurable. Flocculation Ratio was calculated by measuring the initial height of Bentone 38 prior to addition of solvent and then measuring the height of the sediment after solvent had been added. To obtain the Flocculation Ratio final height was divided by initial height. The experiments were run in triplicate and the graph displays the mean Flocculation Ratio and standard deviation (2 sd) error bars.

The following comments may be drawn:

- Flocculation Ratio does not appear to be dependent on the volume of solvent in the system as indicated by effectively constant Flocculation Ratio across the range of test volumes. This could be due to excess solvent to clay mass (0.5g) for each test.

- Flocculation Ratio of Bentone 38 is essentially 1:1 for the silicone fluid system indicating that intercalation of platelets is negligible and that solvent is possibly trapped between agglomerated particles rather than intimate intercalation of platelet layers.

- The Flocculation Ratios for ethanol and propylene carbonate gave an average of approximately 2.5:1 that are over twice recorded for silicone fluid. This would indicate that some intercalation occurs with these polar activators causing the platelets to swell in a polar environment. Neither polar solvent appeared to be more effective than the other.

- The fluctuations of the data at the lower volume systems are likely to be attributed to experimental factors for example, it was difficult to ensure that the clay and solvent had had intrinsic mixing at lower solvent volumes.

3.3.2 Flocculation Ratio at Low Shear Mixing (polar activator diluted)

Figure 3.2 : Graph to show the effect of flocculation ratio at low shear rate (hand shaken) using Clay and Silicone suspensions (1:10 and 1:20 dilutions) with polar activators (between 1% and 20% w/w), n=3

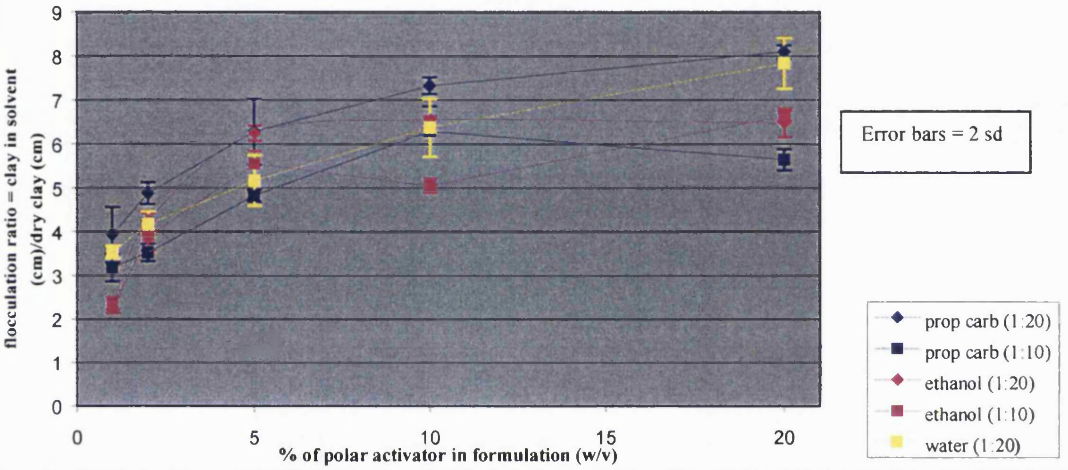


Figure 3.2 shows the results of Bentone 38 in silicone fluid at 1:20 and 1:10 dilutions. Polar activator was added to each dilution at 1, 2, 5 10 and 20 percentage levels (w/w). The graph shows the mean data and standard deviation error bars (2 sd) data for both dilution levels of ethanol and propylene carbonate systems and the 1:20 dilution for the system where water was tested.

The following comments can be made:

- The 1:20 dilution series of clay and silicone fluid and propylene carbonate yields the highest Flocculation Ratios of all the series plotted although the difference is only slight compared to the 1:10 dilution series.

- At low percentages of polar activator (<5%), there is a steep rise in Flocculation Ratio for all the series. Above 5% polar activator concentration, there is a trend for the Flocculation Ratios to increase but the amount that the clay swells is significantly reduced. For example, the series of ethanol (1:20 dilution clay to silicone fluid) at 1% the Flocculation Ratio is approximately 1:2.4; at 5% the Flocculation Ratio increases to approximately 1:6.3; at 20% this ratio has barely increased.

- The series that display the data for the polar activator water appears to show a more linear trend with Flocculation Ratio increasing as the percentage of polar activator is increased in the formulation. Taking into account the standard error, it is possible to plot a straight line through the data points indicating that Flocculation Ratio could be directly proportional to the amount of water added to a formulation. It should be considered that water is highly immiscible with silicone fluid and also has no affinity for the hydrophobic clay and consequently the observations could be due to flocculation of aggregates rather than swelling.

- There is a general trend that the 1:20 dilution series yields slightly higher Flocculation Ratios than the 1:10 dilution series for both propylene carbonate and ethanol. Referring back to Figure 3.1 where polar activators are at 100% level, the Flocculation Ratio was an average of 1:2.5 that is significantly lower than when silicone fluid is present (with Flocculation Ratios being >1:5 at 20% polar activator concentration). It is possible that the silicone fluid aids to disperse aggregates to smaller particle sizes. This would yield a greater clay platelet surface area to be reactive with polar activator. Silicone fluid may also serve as a carrier of polar activator to intercalate between layers.

3.3.3 Flocculation Ratio at High Shear Mixing (Silverson L4R Homogeniser)

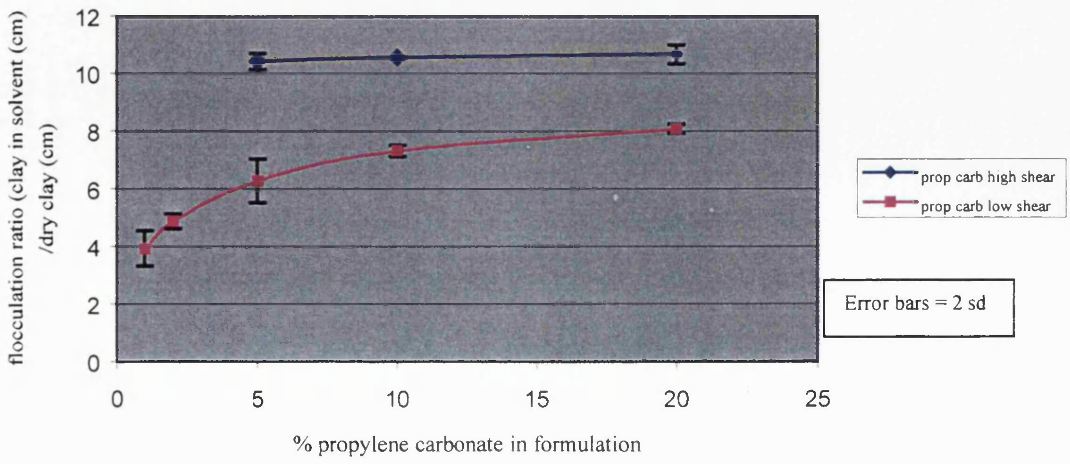
Figure 3.3 displays the mean data of Bentone 38, silicone fluid and propylene carbonate (between 1 – 20% w/w) and the effect of shear rate on the Flocculation Ratio of clay sediment. The error bars indicate 2 standard deviations.

The following comments may be made:

- The effect of high shear mixing with a Silverson L4R rotor/stator homogeniser ($60{,}000s^{-1}$) significantly increases the Flocculation Ratio of Bentone 38 clay in silicone fluid in the presence of polar activator compared to low shear (hand mixing). The Flocculation Ratio for the samples that were subjected to high shear had a ratio in excess of 10:1 compared to that of low shear mixing that was less than 8:1.

- The high shear mixing data series gave fairly constant swelling rate values (approximately 10.5:1) for formulations produced with 5,10 and 20% w/w propylene carbonate. The low shear samples however showed a gradual increase in Flocculation Ratio as the level of polar activator was increased in the formulation. This indicates that the combined relationship of mechanical work and chemical work has a greater efficacy on swelling properties of clay. It also indicates that the Flocculation Ratio is not dependent upon higher levels of polar activator when high shear is applied to the formulations. Conversely, when chemical energy alone is applied, the Flocculation Ratio is dependent upon the level of polar activator.

Figure 3.3 : Graph to show the effect of high shear mixing vs low shear mixing on flocculation ratio of clay in silicone fluid and propylene carbonate (between 1-20%w/w), n=3



Error bars = 2 sd

3.3.4 Effect of Polar Activators on Sedimentation Rate

The previous experiments measured effective Flocculation Ratio of Bentone 38 in the presence of silicone fluid and polar activators by taking the differential in the sedimentation height of solid Bentone 38 in small glass vials. The experiments gave introduction to the effects that polar activators have on swelling properties of clays. There were a number of variables that were not controlled in these experiments.

These included the following:

- All the experiments were run at ambient conditions.

- Control of shear for low shear samples could not measured since the samples were shaken by hand.

- A dip in Silverson Homogeniser was used to shear the high shear samples that means there was no means to guarantee that the mixture had been subjected to the same degree of shear. This could suggest that certain regions of the mixture had continuous shearing while other regions may not have been subjected to any shear.

To control some of these variables, a second stage of sedimentation evaluation was run using a specifically designed laboratory scale rig that enabled temperature control and an in-line single pass homogeniser. The sedimentation measurements were made using measuring cylinders (Class A, tolerance ±0.15ml) instead of glass vials to standardise the dimensions of the test volumes and ensure greater accuracy in sediment height measurement.

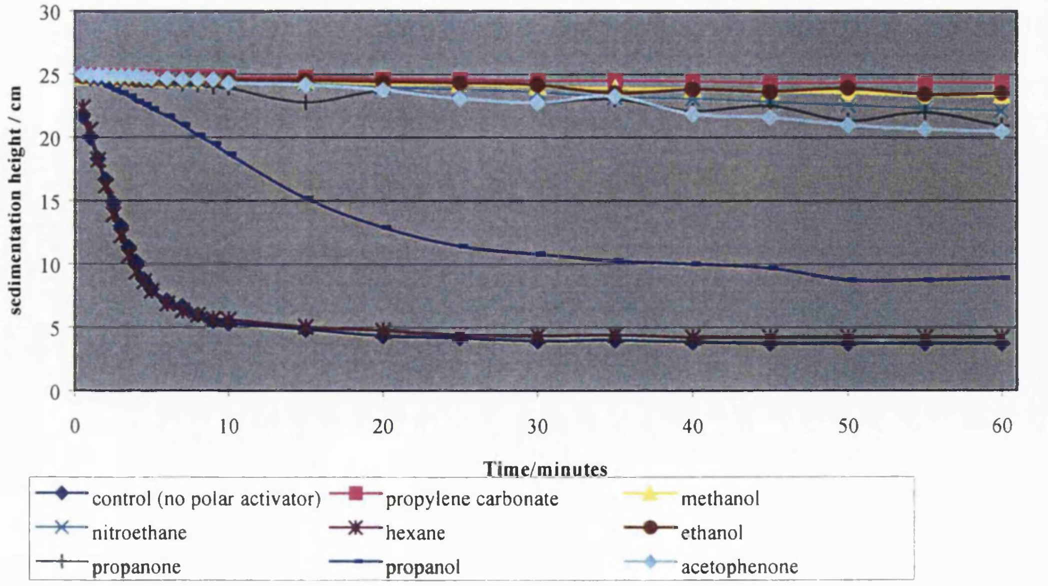
In the following experiments, the actual height of the sediment was recorded rather than measuring the differentials of clay heights to enable calculation of Flocculation Ratio. This was because initial clay height would have had to be estimated since a sample (of the 2 kg batch volume processed) was taken for each sediment height experiment.

3.3.4.1 Rate of Sedimentation (1 Hour)

Figure 3.4 shows the mean sedimentation rate of suspensions over the period of one hour. The following comments can be noted:

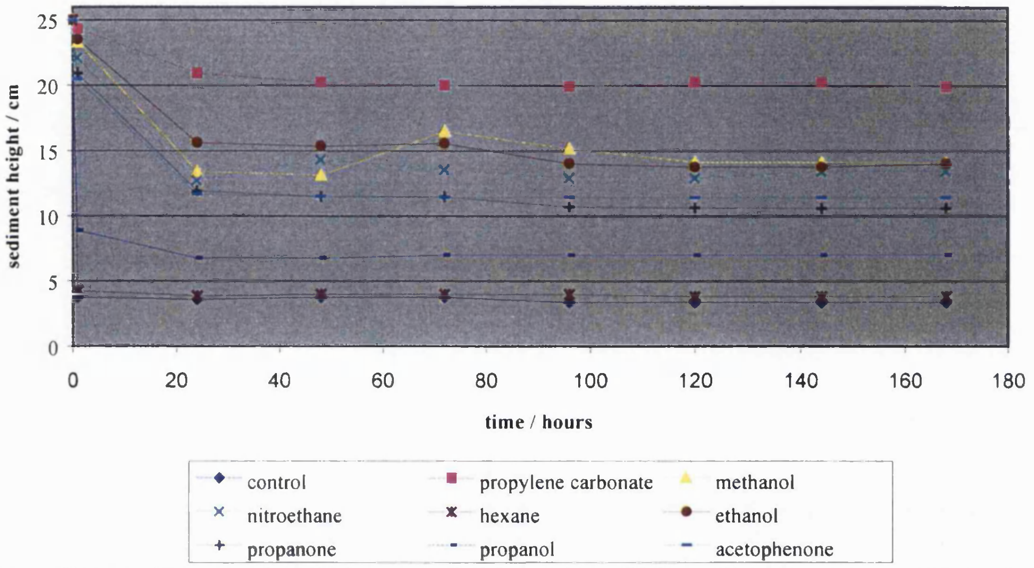
- The graph shows the lower chain alcohols (ethanol and methanol) and propylene carbonate displayed a very slow rate of sedimentation after one hour with little significant difference in sediment height from the start of the experiment. This was also true of the polar activators that carried a carbonyl functional group i.e. propanone and acetophenone and the nitroethane polar activator.
- The control and non-polar activator system, hexane, displayed immediate, rapid sedimentation and a constant sediment height was reached after twenty minutes.
- Propanol was the only polar activator to behave significantly differently from the rest of the polar activators sedimenting at a constant rate for approximately 30 minutes when the sediment level began to plateau.

Figure 3.4 : Mean sedimentation rate of Bentone 38 clay in silicone fluid and polar activator (1%w/w) over time (1 hour), n=5



3.3.4.2 Rate of Sedimentation (1 week)

Figure 3.5 : Graph to show the mean rate of sedimentation of Bentone 38 and silicone fluid with polar activator (1% w/w) over a period of one week, n=5



The data shown in Figure 3.5 shows the effect of sedimentation of the clay over a period of one week. Here the effect of sedimentation for the different polar activators is clearly displayed. After 24 hours the degree of sedimentation becomes constant for all the systems and any further sedimentation may be attributed to compaction rather than sedimentation.

The following may be noted:

- The sediment height of the control and non-polar additive (hexane) reach a constant level almost immediately. This provides a clear picture of sedimentation height (approx. 4 cm) of Bentone 38 without the presence of a polar ingredient.

- It is clear that the most efficient polar activator for a silicone fluid and Bentone 38 mixture is propylene carbonate that undergoes only slight sedimentation reaching a constant level of approximately 20 cm after 48 hours.

- The lower chain alcohols, ethanol and methanol and the nitroethane polar activator are more or less equivalent in respect of final sedimentation heights.

- Comparing propanone and acetophenone to propylene carbonate, all of which carry a carbonyl functional group, it is interesting to observe that the sediment height of the two ketone systems is half that of the carbonate.

- After a week, it is clear to see that propanol stands out on its own as a very poor polar activator. The sediment height of the propanol systems is only slightly greater than the control and non-polar systems.

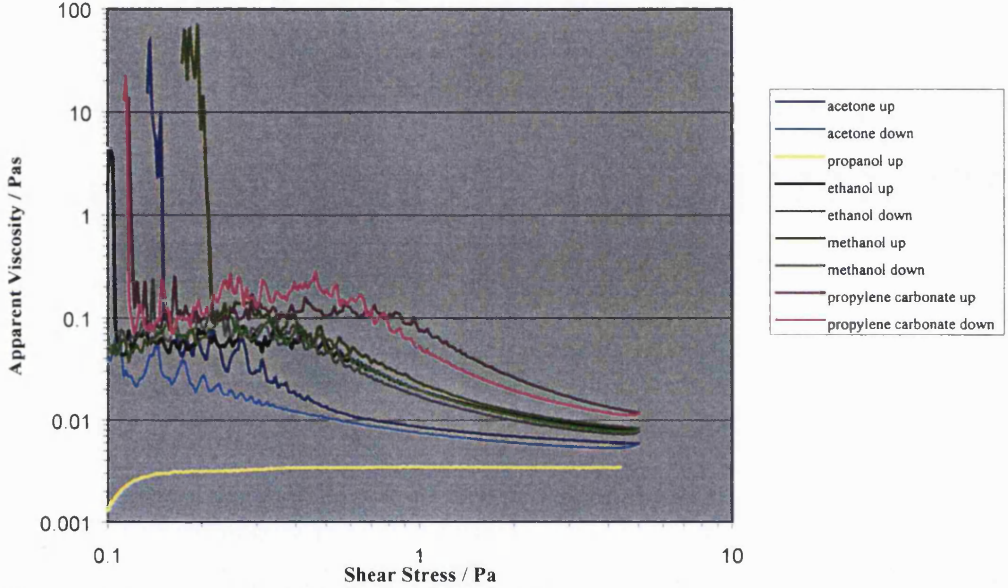
The results for the systems measured after one month are not displayed since there was no further sedimentation noted.

3.3.4.3 Rheological Measurement of Bentone 38 Suspensions with Polar Activators

In addition to sedimentation rates, each sample was analysed using the Carri-Med Rheometer. Each test was completed one hour post manufacture and after the first hour of settling measurements had been taken. Prior to loading the product sample onto the Carri-Med, the sample was shaken lightly to resuspend any materials that had started to settle.

Figure 3.6 shows representative results of a series of flow curves created by plotting viscosity against shear stress. The graph details of the alcohol group polar activators (methanol, ethanol and propanol) against the carbonyl group polar activators (propylene carbonate and propanone). It was not possible to obtain rheological profiles for the control sample or hexane activator since the samples had sedimented during the equipment set up procedure was completed and thus the results were not representative of the system.

Figure 3.6 : Rheological Profile of Bentone 38, silicone fluid and polar activator (1%) measuring viscosity (Pas) against shear stress (Pa) - up and down curves



The following comments may be made:

- Ramping shear stress up to 5 Pa had a slight lowering of viscosity for all the samples with the exception of propanol for which only the ‘up curve’ could be recorded.

- Reducing the shear stress the samples recovered and viscosity began to build as would be expected for a thixotropic liquid.

- A down curve was not achievable for either of the control samples or propanol since the clay had already sedimented in the time taken for the experiment to run and the plate was simply measuring the slip of silicone fluid recording an error and thus terminating the run automatically.

- The samples prepared with propylene carbonate were found to be the most stable yielding the highest viscosities with increased stress.

- The samples manufactured with ethanol and methanol gave almost identical profiles as with the sedimentation height study with propanone ranking next in order. These results correlate with the results obtained in the sedimentation studies.

This technique was concluded not to be the optimum method for recording the rheological profile of clay suspensions. This was because each of the suspensions test was prone to very rapid sedimentation and therefore it is possible that wall effects and other such factors as described in Chapter Two would have effected the results. Using concentric cylinder geometries may have reduced the effects of sedimentation. Nevertheless, within practical reason, each test suspension was exposed to the same test conditions and this experiment validated the apparent viscosity rank order of each polar activator.

3.3.4.4 Brookfield Viscosity Measurements

The viscosities of the samples were also measured using the Brookfield Viscometer and the results are shown in Table 3.1. Viscosity measurements were recorded immediately after processing. A small sample of test fluid was collected in a beaker at the start of the final pass through the homogeniser and viscosity was measured while the remaining mixture of the 2-kg batch was being processed. This ensured that viscosity was recorded at zero time when sedimentation was at a minimum.

Table 3.1 displays the mean viscosities of each of the systems measured using a Brookfield Viscometer with a Helipath attached. The T-bar spindle (spindle A) was used for each measurement and the rotation speed was set to 10 rpm.

N.B. Viscosity measurements were recorded in centipoise (cP).
$1cP = 10^{-3}$ Pa.s

Polar Additive	**Viscosity* / cP**
Propylene Carbonate	400
Ethanol	160
Methanol	220
Propanol	60
Propanone	100
Acetophenone	108
Nitroethane	156
Hexane	45
No additive (Control)	40

* Average viscosity (TA Spindle @10rpm)

Table 3.1: Mean viscosity measurements (cP) of Bentone 38 suspensions

The following comments may be made:

- Propylene carbonate systems yielded the highest viscosity measurement of the series at 400cP. This was almost double the value of the next most viscous system (methanol, 220cP).

- The lower chain alcohols (ethanol and methanol) and the nitroethane polar activators were the second most viscous samples in the series. Propanol however, was significantly different from the other alcohols tested and ranked closer to the non-polar and control samples in its viscosity at 60cP.

- The control sample and the non-polar hexane series yielded the lowest product viscosities of 40 and 45cP respectively.

- The two ketone series (propanone and acetophenone) had viscosities of approximately 100cP.

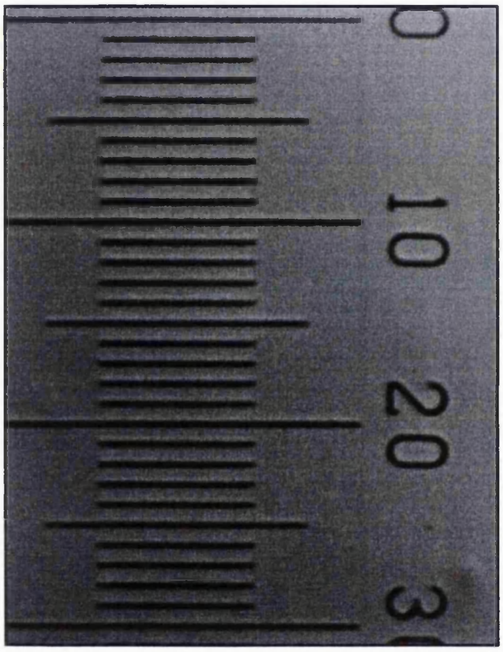
A comment should be made with regards to the Brookfield Viscometer measurements. As the spindle rotates through the sample, the shear exerted via the spindle will destroy any network form by a certain degree. This is why the Helipath is utilised since the spindle 'sees' a fresh sample as the Helipath lowers through the mixture. Nevertheless, it is unwise to use Brookfield Viscosity measurements as absolute and they should serve as an indication and to corroborate other results. It is possible to conclude that the results obtained in this experiment do reinforce the observations made from the other experiments in this series.

3.3.4.5 Optical Microscopy

Each set of samples was imaged using conventional optical microscopy. For each experiment at least six images were captured to ensure sampling was representative. The images shown in Figures 3.7 to 3.16 represent micrographs selected from each polar activator or additive series. The images have been scanned maintaining aspect ratio and dimension constant to allow comparison. The graticule (Figure 3.7) has also been included to provide a scale.

Control Sample (Figure 3.8)

The image of the control sample shows a range of particle sizes, the larger entities being agglomerates of Bentone 38 clay. The larger agglomerates are of dimensions between 30 and 40 μm. The large agglomerates predominate in the sample with only a small proportion of smaller agglomerates of less than 10μm being present.



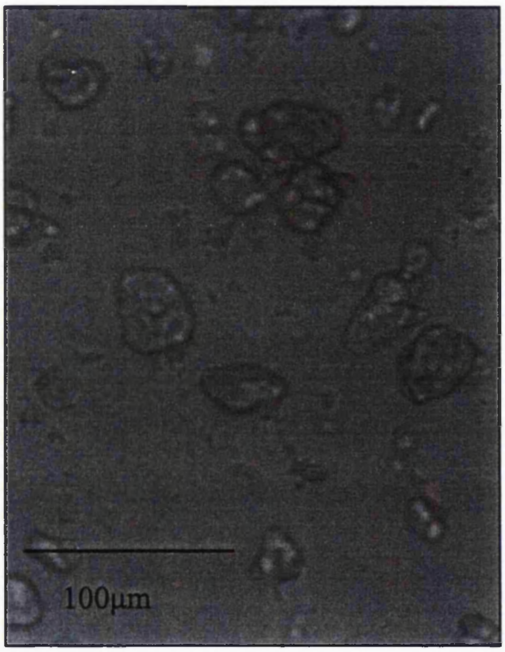
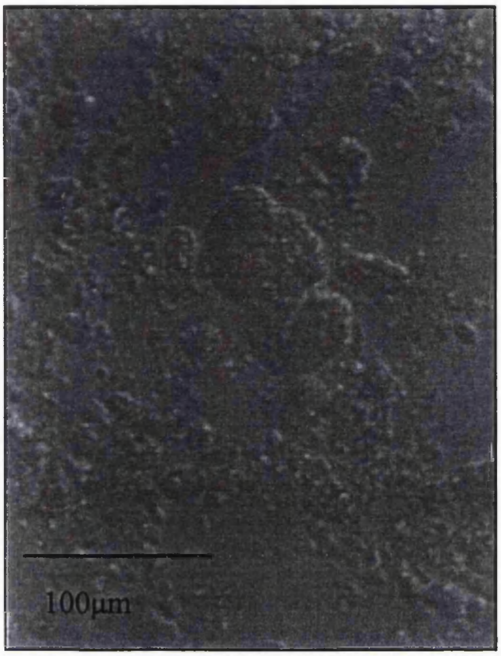


Figure 3.7 : Micrograph of Graticule 0-10 represents 100µm (x20 DIC)
Figure 3.8: Micrograph of control sample (Bentone 38 and Silicone Fluid only) (x20DIC)

Propylene Carbonate (Figure 3.9)

It would be expected that the propylene carbonate sample would be significantly different than the rest of the images and it is possible to say that there appears to be a greater number of smaller particles present (<10µm). However, the micrograph clearly shows a very large agglomerate (~80µm in length) present indicating that a fully dispersed system has not been achieved.



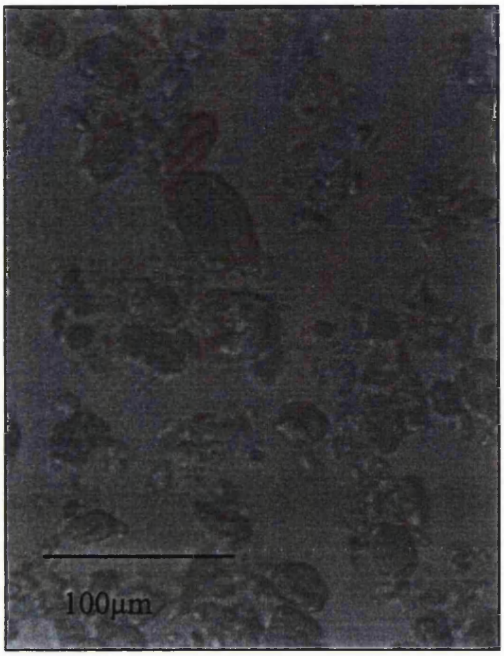
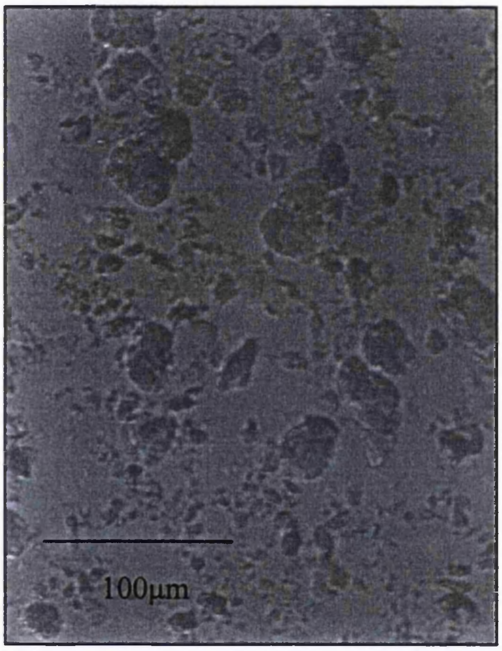


Figure 3.9: Micrograph of propylene carbonate sample (x20 DIC)
Figure 3.10: Micrograph of methanol sample (x20 DIC)

The presence of a greater number of smaller particles correlates to the observations of increased viscosity in both the Brookfield Viscometer measurements and the highest stability from the rheological profile. It also correlates with sedimentation study where the propylene carbonate series had the slowest rate of sedimentation. The distribution of smaller agglomerates would have two effects. Firstly, the surface area of particles increases as distribution of particle number increases therefore there would be greater interparticle attractions and thus a more stable and viscous system. Secondly, as the agglomerates have been broken into smaller particles, there would be an increase in volume of space occupied by the particles.

Methanol (Figure 3.10)

There is a wide range of agglomerate sizes present in the series produced with methanol. They range from a small number of particles of <10μm to particles of 50μm. The majority of particles appear to be in the range of ~30μm.



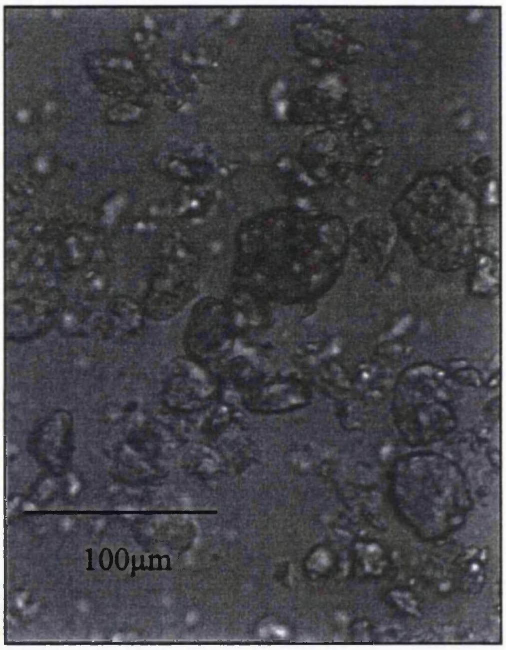


Figure 3.11: Micrograph of ethanol sample (x20 DIC)

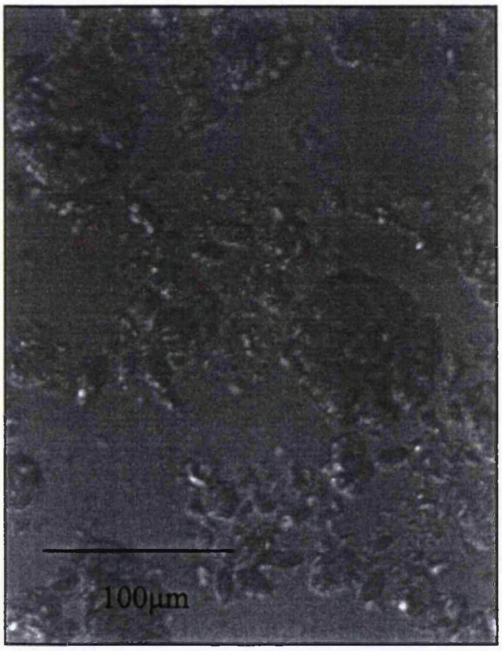
Figure 3.12 : Micrograph of propanone sample (x20 DIC)

Ethanol (Figure 3.11)

The series manufactured with ethanol polar activator also display a wide range of particle sizes. There appears however, to be a greater proportion of smaller agglomerates of <10μm than in the sample produced with methanol. There is however a significant proportion of larger agglomerates present ranging in size up to 50μm.

Propanone (Figure 3.12)

The micrograph representing the samples produced with propanone polar activator display that there was a greater proportion of large agglomerates of dimensions ~50μm diameter to smaller agglomerates.



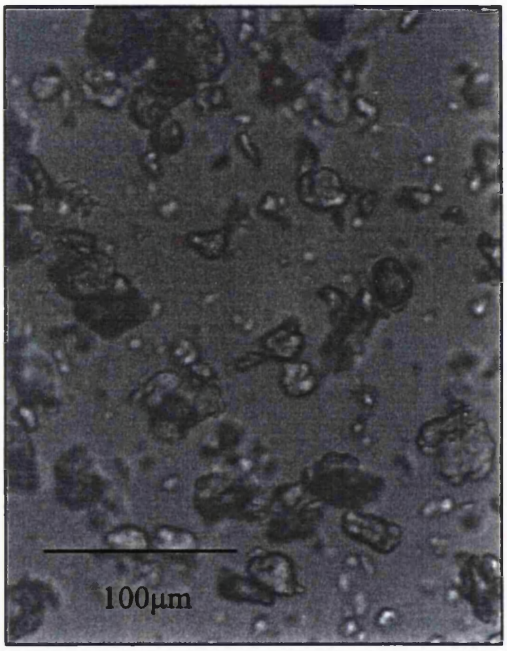


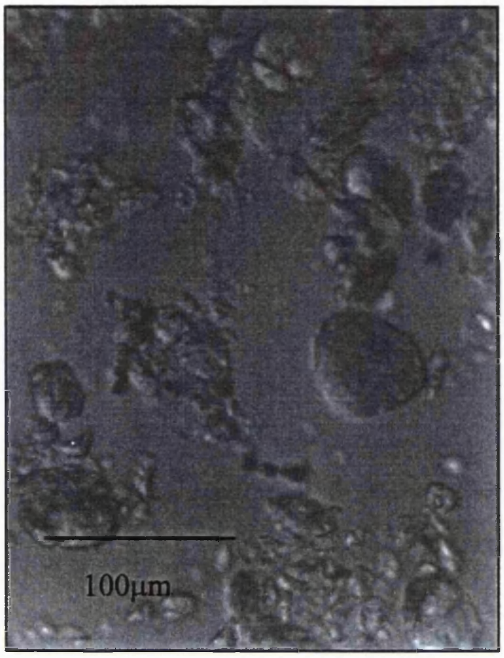
Figure 3.13 : Micrograph of nitroethane sample (x20 DIC)
Figure 3.14 : Micrograph of hexane sample (x20 DIC)

Nitroethane (Figure 3.13)

The image of the sample produced with nitroethane clearly displays very large agglomerates of dimensions between 70 and 80μm in diameter. There is also a significant proportion of smaller particles present that are approximately 20μm in diameter.

Hexane (Figure 3.14)

The micrograph of the sample made with hexane displayed particles of similar nature to those of the control sample in Figure 3.8. This would be expected since hexane is non-polar. There is a low proportion of small agglomerates also present.



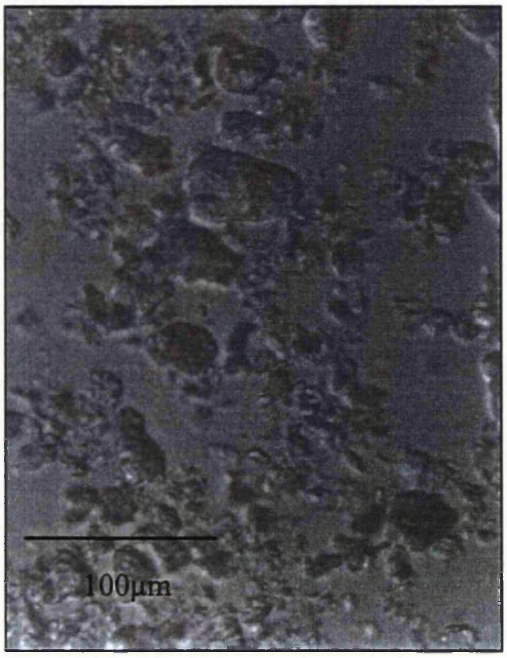


Figure 3.15: Micrograph of propanol sample (x20 DIC)
Figure 3.16 : Micrograph of acetophenone sample (x20DIC)

Propanol (Figure 3.15)

The image of the sample manufactured with propanol displays the presence of large agglomerates of dimensions ~50μm in diameter. There are also a significant number of smaller agglomerates ~20μm also present. There do not appear to be significant numbers of agglomerates or particles of dimension <10μm present.

Acetophenone (Figure 3.16)

The micrograph of the sample that was made with acetophenone shows that there is a wide distribution of particle sizes present. A significant proportion of the particles are of dimensions ~10μm however they range in size up to 50μm.

The images in all these micrographs display that it is difficult to correlate particle size to stability and viscosity of this series of polar activator with the exception of propylene carbonate where the presence of a greater distribution of small agglomerates is noticeable. It is however possible to determine that the shear rate of the Silverson Homogeniser (after 5 passes) in the presence of polar activator does not fully disperse or delaminate clay platelets in silicone fluid as seen by the presence of a significant number of large agglomerates present in all samples.

The presence of large agglomerates could be the reason why significant settling and sedimentation is noted for all the systems made using this process. The network formed by these agglomerates may not yield strong enough attractive forces to overcome the forces of gravity that would be responsible for the larger agglomerates to settle in the system. It is therefore reasonable to assume that sedimentation is a consequence of particle size.

It is not possible to draw conclusions of the effectiveness of polar activator from the micrographs since there are no obvious differences from sample to sample. All display a wide range of particle size distribution but there is no evidence of a structured network of particles formed.

3.3.4.6 Visual Observations and Comments

All the systems regardless of polarity of activator were prone to sedimentation over time. The systems had all reached equilibrium within 48 hours of manufacture after which, only slight insignificant compaction occurred. None of the systems formed a 'gel' that is described in the literature despite following a strict processing regime where all the Bentone 38 was intrinsically mixed with a high shear engine and polar activator. The systems could be described as viscous liquids prone to gross syneresis of silicone fluid and therefore highly unstable over time.

Propylene Carbonate was clearly the most effective polar active ingredient with the lower alcohols (ethanol and methanol) ranking next in order. The propanol series proved to be the anomaly of the set, yielding very unstable networks and would indicate that it is a very poor polar activator in its own right. It is possible that propanol is too large in molecular dimensions to intercalate between the platelet layers and migrates to the outer surfaces of agglomerates and encourages agglomeration rather than delamination.

As expected, the control and the non-polar additive (hexane) gave rise to rapid sedimentation, highlighting the instability of Bentone 38 systems in the presence of silicone oil despite mechanical energy being applied. It also complements the literature review that polar activators are required for enabling a network formation. (Schaefer et al, 1971; Cody and Reichert, 1986; Kemmetz et al, 1989).

Neither could it be claimed that a fully dispersed system had been achieved using a high shear homogeniser. This contradicts the literature (Rheox Ltd, Rheox Handbook) that claims that a fully dispersed system can be achieved using dispersing aids (e.g. Cowles blade, tri-homo mills) which impart a lower shear rate than that applied using a Silverson L4R homogeniser. The microscope images also confirm that agglomerates were evident for all samples, regardless of polar activator, correlating the evidence that a fully dispersed system was not achieved.

The study indicates that polar activators can play a role in gelation by interacting with the clay. However from these results alone it is not possible to positively identify how this interaction occurs. It is postulated that dispersion is directly related to the solubility of the quaternary ammonium compound in the solvents used. This would account for why no swelling and rapid sedimentation was observed for hexane since the hydrocarbon chains of the quaternary ammonium compound are not solvated to any significant extent in hydrocarbons. It is possible that the polar activators used in this study interact with the head group of the quaternary compound.

Work performed by Burba & McAtee (1981) has shown that with certain organophilic clays, polar activators can lift the aliphatic chains from the surface of the clay and increase the basal spacings. Their work focused on single chain compounds on the surface of clay, however it is probable that a similar effect would be observed with double-chain quaternary ammonium compounds. They claim that the effectiveness of intercalation is dependent on the surface coverage of the amine and at this time it is not understood why swelling does not occur at very low and very high surface coverage.

To summarise, Bentone 38 is not dispersed effectively by chemical activator alone. Chemical activators do interact with the clay to varying degrees depending upon the activator selected. With the aid of shear, sedimentation rate is reduced with the addition of polar activators but the shear applied using a Silverson Homogeniser is not sufficient to break up the agglomerates to primary particles.

In order to provide a more comprehensive understanding of the polar activator's interaction with clay two detailed studies were also carried out:

- Surface Force Analysis to determine the affinity of polar activators and solvents to the surface of clay.
- Electrophoresis to determine the electric properties of the clay and their interaction with different polar groups.

By having an understanding of the electrical properties of the basic ingredients in the formulation and an understanding of the affinity of polar molecules to the surface of clays, would provide a better insight into the role of activators on gelation.

3.4 Surface Force Measurement

3.4.1 Forward

The Surface Force Measurement Apparatus (SFM) is capable of measuring the forces between two molecularly smooth surfaces in liquids. It is also capable of measuring the refractive index of the medium between the surfaces, adsorption isotherm, capillary condensation and surface deformations arising from surface forces. Mica sheets are primarily used in this technique since, once cleaved they are molecularly smooth, however, it is possible to coat the surfaces with surfactants, polymers, metals etc thus altering the nature and chemistry of the interacting surfaces while keeping them smooth by virtue of the mica substrate surface beneath.

3.4.2 Aim of Work

The aim of this work was to measure the surface forces between mica sheets coated with the quaternary ammonium compound (dimethyl dioctodecyl ammonium chloride, Arquad – 2HT) in a silicone fluid environment and dosing the systems with varying layers of propylene carbonate. However, time restrictions due to availability of equipment allowed only the study of mica in silicone fluid DC1465 with water and propylene carbonate to be carried out.

Mica serves as a model clay for Bentone 38 clay being a 2:1 dioctahedral clay mineral with a chemical structure similar to montmorillonite clay.

3.4.3 Background to Previous Studies of SFM

Most SFM studies have concentrated on aqueous systems and the effects of hydrated ions, polymers and surfactant films on the force–distance curve between mica surfaces. This is widely documented in standard colloidal chemistry texts (Hunter, 1989; Evans and Wennerstrom, 1994). For non-aqueous environments the focus is mainly on the solvation forces. In particular, there are several studies addressing the solvation layers in octamethylcyclotetrasiloxane (OMCTS), a D4 silicone fluid (see Chapter 2). N.B. The silicone fluid used in this study is a 1:1 mixture of D4 and D5.

In non-polar liquids, like silicone fluids with low dielectric constants (~2), electrolytes do not dissociate. Christenson and Horn (1985) quote that a double layer force is not expected between mica sheets and neither is one observed. The only interaction between mica sheets that would be predicted by the continuum theory is the van der Waals force of attraction. Christenson and Horn (1985) however did not observe this in their results.

Figure 3.17 shows typical data reproduced from Christenson and Horn (1985) that shows as mica surfaces approach, there is at first a weak attraction in accord with the Lifshitz theory (Hunter, 1989) of the van der Waals force; but at separations less than 2-10 nm, the force becomes an oscillatory function of distance, alternating between repulsive maxima and attractive minima. The solid lines represent stable parts of the force curve and the dashed line represents regions of instability.

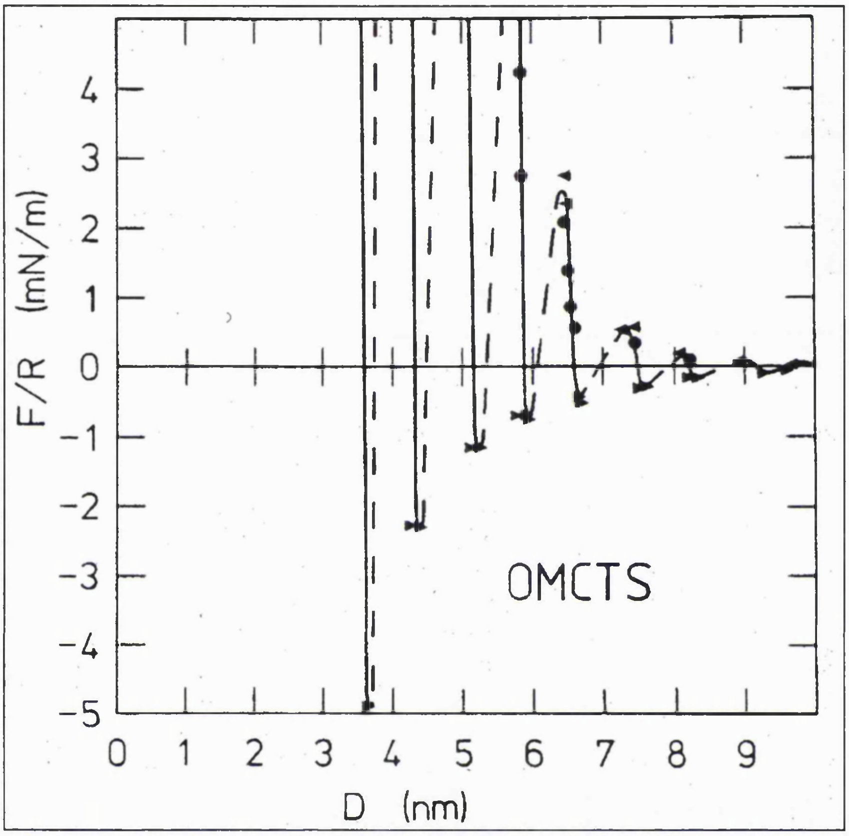


Figure 3.17 : Force-distance curve for anhydrous OMCTS (D4) silicone fluid between mica. Note the oscillatory nature of the data (reproduced from Christenson and Horn, 1985).

The key points to note are:

- Even at separations as low as 9 nm, there is no long-range repulsion and the force measured is virtually zero. This indicates that there is no ionisation of the mica surfaces.
- The force begins to oscillate with amplitude increasing with decreasing separations. These oscillations are believed to be attributed to removal of solvation layers of roughly spherical D4 molecules as the surfaces become closer together. The large contact area between the molecularly smooth sheets results in packing of the

molecules. Increasingly large forces are required to eliminate each layer of OMCTS.

- The mica sheets do not recover to zero separation and appear to be unable to move with 3.5 nm separation. It is concluded that since the molecular diameter of D4 is approximately 0.9nm, approximately four layers of molecules are closely packed between the surfaces.

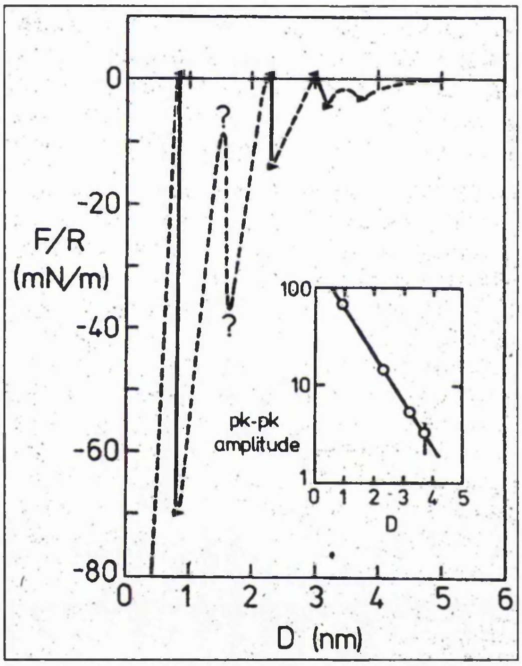


Figure 3.18 : Effect of a water saturation of 0.5 on the surface forces in OMCTS (reproduced from Horn and Israelachvili,1981).

Studies were also made for binary systems of D4 and cyclohexane (Christenson, 1895). It was found that the periodic nature of the solvation force and its range were both reduced when the liquid phase consists of molecules of different diameter although a large barrier to reaching full contact was still present at single molecule separations. Since Silicone fluid DC 1465 is just such a binary mixture, the well-defined oscillations seen in figure 3.17 would not be expected.

Studies on non-aqueous systems have highlighted the significant effect trace quantities of water have on surface forces and on forces required to separate mica surfaces in primary contact. Water, itself a highly polar molecule, is likely to be present in all systems. Figure 3.18 shows the effect of allowing water to enter the environment. Further saturation caused further depression of the curve with the surfaces moving into contact from greater separations. In addition the separation on contact also increase, implying the water builds up at the mica surfaces. Disruption of the oscillatory nature of the force curve and the stronger attraction at a distance was attributed to the binary molecule packing effect where even trace quantities of water were seen to be capable of disrupting the solvation layers.

3.5 Surface Force Measurement of Clay

3.5.1 Surface Force Measurement Apparatus

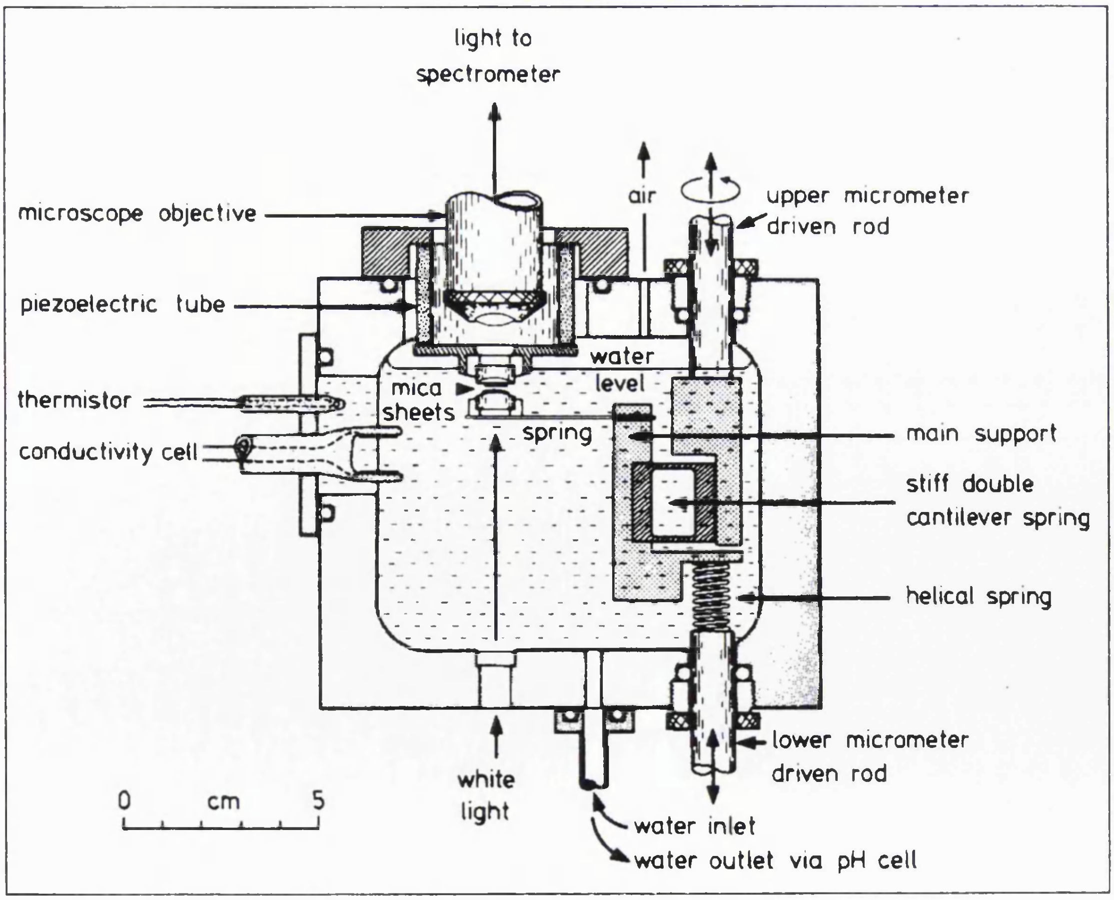


Figure 3.19 : Diagram of the SFM apparatus (reproduced from Hunter, 1995)

The dynamic SFM apparatus used in this study is situated in the Centre for Interfacial Engineering, University of Minnesota, U.S. and Peter Carew (Unilever Research Port Sunlight) kindly performed the experiments. The equipment is virtually identical to normal SFM units described in standard texts (Hunter, 1986; Evans and Wennerstrom, 1994) and detailed by Israelachvili, 1973. The key difference between the dynamic and normal units is the option to oscillate one lens in the lateral direction and to measure the frictional force transmitted by the fluid on the other (Luckham and Manimaaran, 1997).

Figure 3.19 shows a diagram of the SFM unit. Force is measured between two mica surfaces in the configuration of cross cylinders by expanding or contracting the piezoelectric crystal tube by a known amount and then measuring the distance the two surfaces have moved. The surfaces consist of two mica sheets silvered on the back and mounted onto silica discs. The separation is measured by constructing a multiple-beam interferometer with silvered mica sheets. White light entering the gap from the bottom experiences multiple reflections between the surfaces, emerging only at discrete wavelengths.

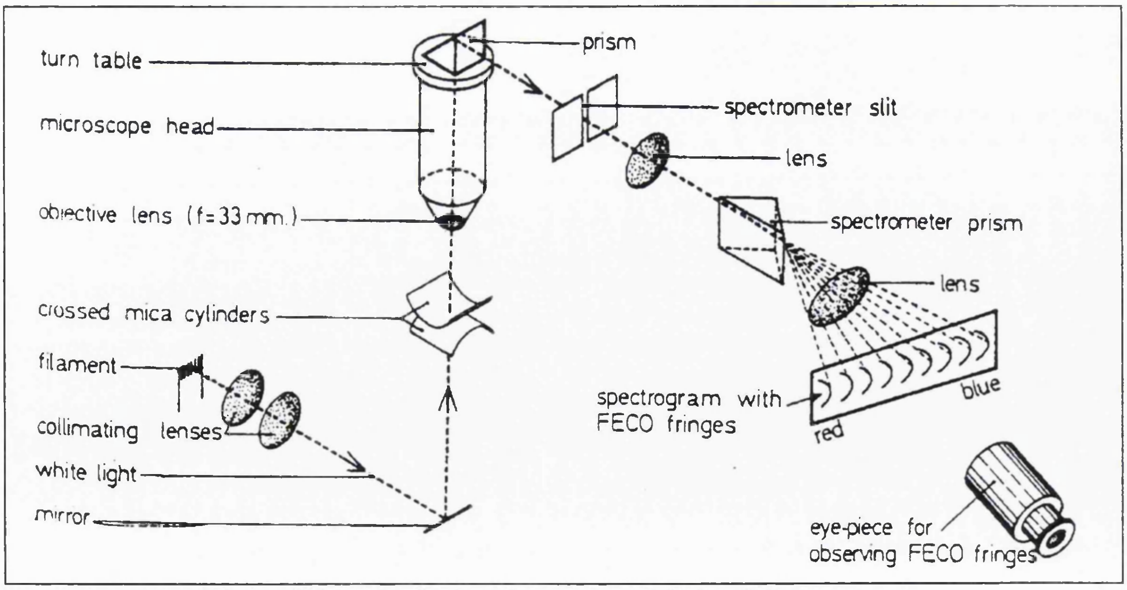


Figure 3.20 : Optical pathway through the SFM apparatus (reproduced from Israelachvili, 1973)

Figure 3.20 shows the schematic path of light in the SFM apparatus. The three-layer interferometer formed between the two cylindrical sheets of mica and the thin solvent film causes the white light to produce Fringes of Equal Chromatic Order (FECO). As the mica sheets approach each other, the film thins and the fringes viewed by the spectrometer shift. Resolving these determines the separation of the sheets.

The lower mica surface is connected through a leaf spring to a clamp via a double cantilever spring and precision potentiometer. As the surfaces are brought together from a large separation, the leaf spring must deflect toward contact in order to balance the attractive force.

Taking the stiffness of the force measuring spring and multiplying it by the difference in the two values of the surface gives the force difference between the initial and final positions. Both repulsive and attractive forces can be measured.

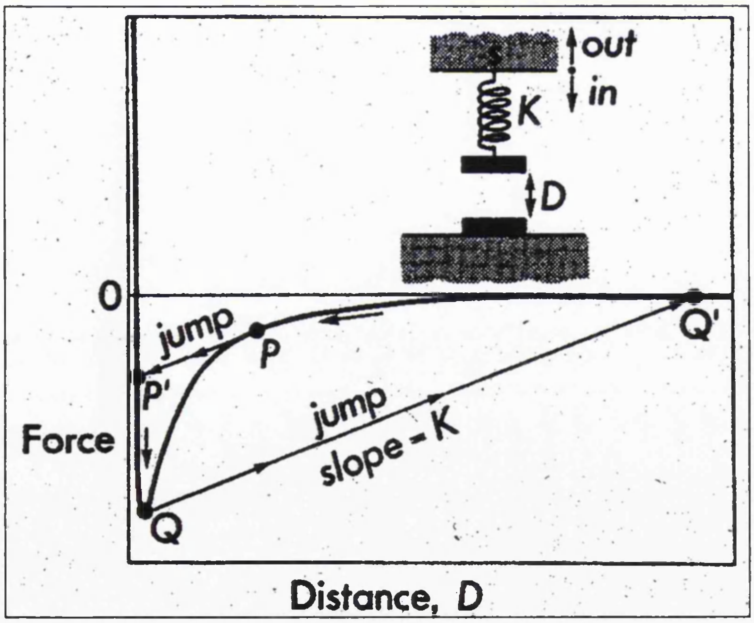


Figure 3.21 : Schematic representation detailing how certain regions in the force distance curve may be inaccessible. At a separation (P) the attractive force gradient exceeds the spring constant and the surfaces jump into contact (P'). When the surfaces are separated, they spring back from Q to Q'. The adhesion energy is obtained from force at Q (reproduced from Horn and Israelachvili, 1981)

Figure 3.21 shows a schematic representation of two sheets experiencing separation and adhesion. At point Q', the mica surfaces are separated by a distance D. As these surfaces are moved closer together a force gradient is observed. At a point P the force gradient exceeds the spring constant K and the surfaces snap into contact represented on the diagram as P jump to P'. As the surfaces are separated once more, a second 'jump' is observed from Q to Q'. The adhesion energy is obtained from the force at Q. (Horn and Israelachvili, 1981).

3.5.2 SFM Experimental Studies

3.5.2.1 Preparation of Silicone Fluid and Propylene Carbonate

The silicone fluid (DC1465) and Propylene carbonate were dried by storing over a molecular sieve (4 Å) for one week and filtered through a 0.2 μm syringe filter.

To examine the role of propylene carbonate and water on the forces measured between the mica sheets, the dried silicone fluid was mixed with propylene carbonate or water to produce saturated solutions. These were then diluted to produce a range of different saturated levels. A slow saturation method was also used in which a small open vial of propylene carbonate or water was placed within the sealed box with the initially dry silicone fluid thin film. Force distance curves were then taken over frequent intervals to monitor the effect of saturating the thin silicone fluid film with polar liquid.

3.5.2.2 Preparation of Mica Sheets

A thin sheet of Mica is first cleaved from a thick mica plate. Cleavage is initiated by inserting the tip of a sharp needle into the edge of the plate and carefully peeling away thin sheets.

A freshly cleaved sheet is examined in the light of a fluorescent lamp. If the sheet is sufficiently thin, interference colours are seen reflected by the surface. These colours change abruptly at cleavage steps, but remain uniform over regions of constant thickness. Two small square sheets (0.5 cm x 0.5 cm) are cut out using a hot platinum wire. As each square is cut, it is placed on a large sheet of freshly cleaved mica. To prevent contamination, gloves are worn, forceps are used to handle the mica and the procedure is carried out in a laminar flow dust free cabinet.

The exposed surfaces are then silvered in an evaporator at a pressure of ~ 10^{-5} τ. A pure, uniform layer of silver, ~400 – 500 Å thick is deposited on the mica surface. The mica surface is glued to two silica discs using sym-diphenylcarbazide glue. Sym-diphenylcarbazide glue is used since it is suitable for use in non-polar solvents.

3.5.2.3 Experimental Methodology

The sheets were mounted in the apparatus and approximately 1 ml of silicone fluid (DC 1465) was added to the gap between the mica sheets using a syringe needle before the SFM box was sealed. The mica sheets were pulled out of primary contact and the system was allowed to reach equilibrium.

The mica surfaces were separated to a gap of approximately 1 μm and then gradually brought closer together by use of the calibrated stepper motor. The distance was measured by following and counting the fringes as they passed the eyepiece.

The following systems were analysed:

1. Mica and Dry Silicone Fluid (DC1465)
2. Mica and Water saturated Silicone Fluid (DC 1465)
3. Mica and Propylene Carbonate saturated Silicone Fluid (DC 1465)
4. Mica coated with quaternary ammonium chloride (Arquad 2HT) and dry DC 1465

3.6 SFM Results

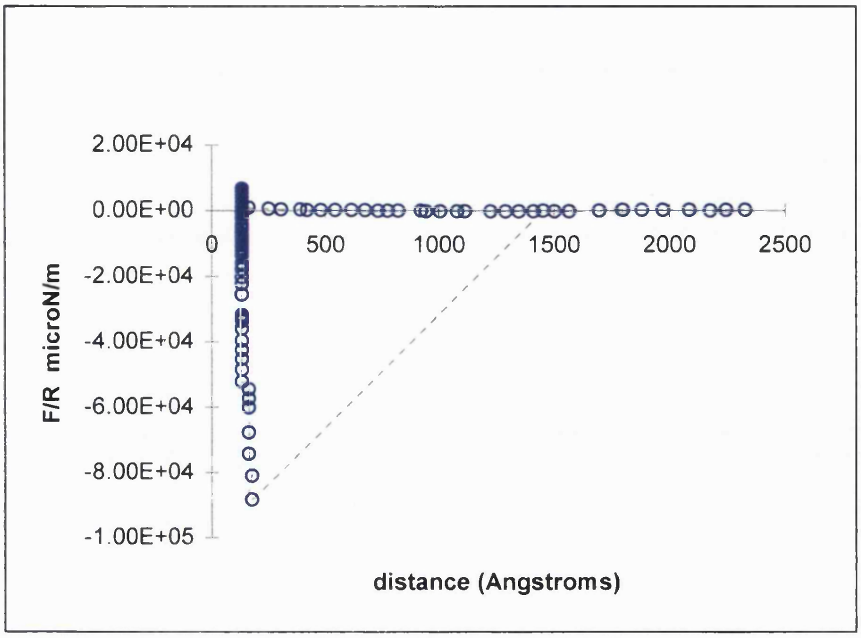


Figure 3.22 : Force-distance curve for dry silicone fluid between bare mica sheets.

Figure 3.22 is representative of the typical the force distance data obtained for mica and silicone fluid (DC 1465). It should be noted that the graph shows the complete absence of any repulsive forces as the separation reduces. In addition, the surfaces do not return to zero separation when in contact that implies the existence of a barrier. Figure 3.23 is the similar data plotted on a logarithmic scale with theoretical data of van der Waals curve for Silicone fluid and the OMCTS solvation force curve (Christenson and Horn, 1985). The solvation curve is based on the diameter of the OCMTS molecule. The theoretical data for OCMTS was included to highlight the absence of repulsive forces between the mica sheets in the presence of silicone fluid.

As the mica sheets approached contact, there was no measurable retardation indicative of a repulsive force. At approximately 50Å, the surfaces snapped into contact under the influence of short-range van der Waals forces of attraction. In the environment of silicone fluid, a non zero contact was established indicating the presence of a steric barrier which could have been a result of a number of mechanisms:

- A solvation layer was formed from a number of layers of the spherical D4 and D5 present in silicone fluid DC1465. The detail of how this occurred is referred to earlier in this section. (Christenson and Horn, 1985)
- The surface could become increasingly saturated with water molecules that promote a more rigid barrier. This is plausible based on prior work (Christenson, 1985) that suggests oscillations are more difficult to visualise in a binary oil system and in systems where water saturation is significant. Both effects were present in the experiment.
- There could be the presence of higher molecular weight silicone fluids in the silicone fluid (DC1465) that were attracted to the surface of the mica.

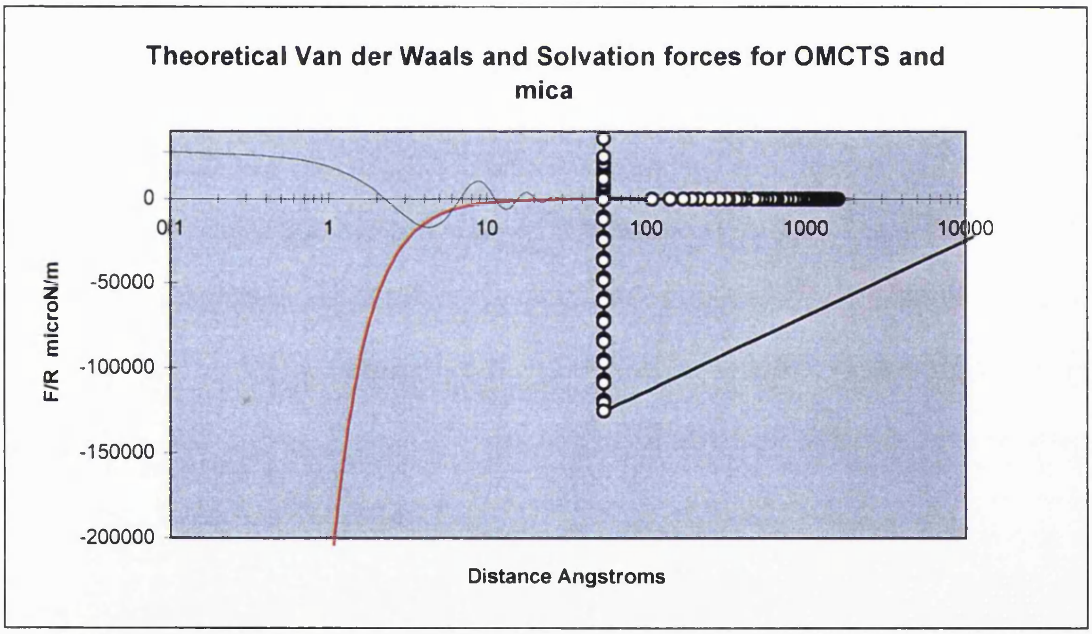


Figure 3.23 : Force distance data and theory for OMCTS and DC1465. The van der Waals curve (red) is based on literature data for silicone fluid. The solvation force curve (black) is based on the diameter of the OMCTS molecule.

Figure 3.24 shows the repeatability of the data for the dry silicone fluid system. The graph displays force curve data from three independent experiments. In particular, the repeatability of the force required to overcome the contact adhesion (magnitude of force curve = -9×10^4 microN/m) is evident. In addition, the graph shows that for each experiment, a non-zero contact was obtained indicating that the boundary formed between the mica sheets remained constant with the silicone fluid used. It should be also noted the amount of force the sheets were subjected to by data above zero force axis had no effect on overcoming the film barrier between the mica sheets.

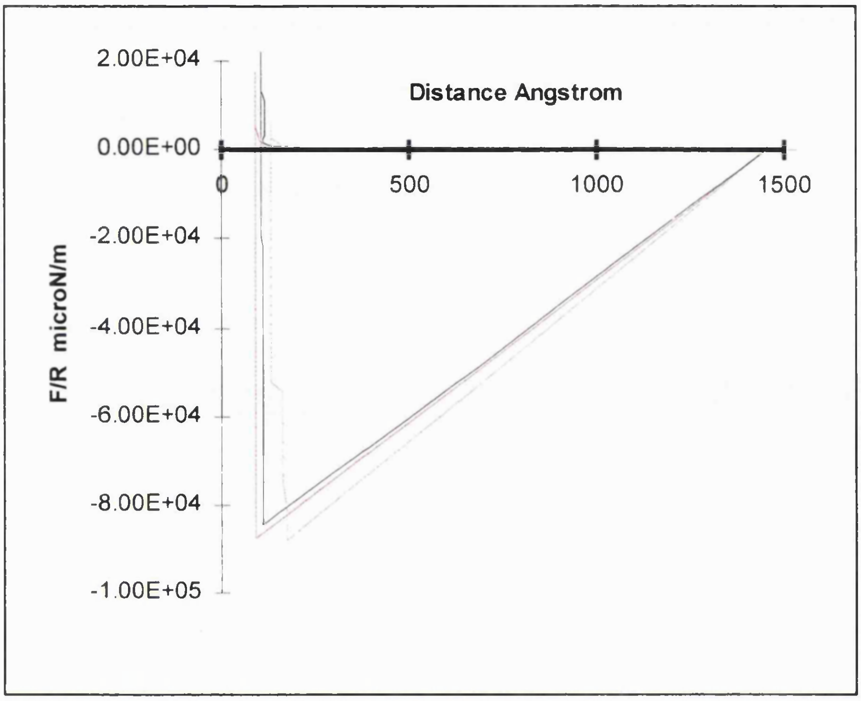


Figure 3.24 : Data from repeated tests for ‘dry’ silicone fluid between bare mica.

Propylene Carbonate and Water were then introduced to the system (described earlier) by saturating the silicone fluid using a small open vial of the polar liquid placed in the SFM box. Measurements were carried out at intervals (between 0 and 36 hours) to ensure sufficient polar activator had been introduced. The results are presented in Figures 3.25, 3.26 and 3.27.

Figure 3.25 shows the force distance data for silicone fluid exposed to propylene carbonate or water vapour for different exposure periods. It should be noted that all the curves were very similar with the exception of the 24h water data that could imply the appearance of a second phase on the surface of the mica. It is difficult to determine whether there were significant differences from this plot and therefore the same data was replotted using an expanded force axis (Figure 3.26).

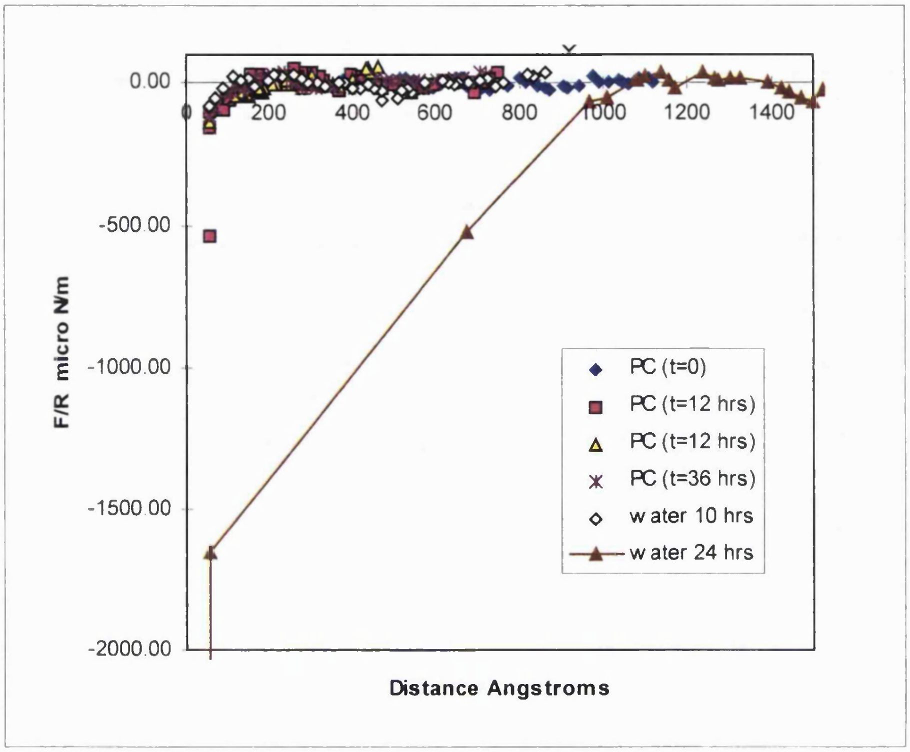


Figure 3.25 : Force distance data for silicone fluid exposed to different periods to propylene carbonate and water vapour.

The first point to note is the general absence of any repulsive feature on the force distance curve. It should be noted that the units of the Force/Lens radius axis are in micro N/m thus any undulations could be within the experimental error that would be associated with the servo motor calibration. However, it can be said that just prior to contact of the mica sheets, there appears to be a slight concentration of data above the zero force axis. This would indicate short range repulsion forces however these data are not deemed to be significant based on the experimental results obtained by Christenson (1985) for pure OCMTS where clear oscillations were obtained. The only data set that stands out is that for the silicone fluid saturated with water (24 hours). It would appear that a different mechanism is acting here. For example, bulk phase separation of immiscible water and silicone fluids that could be caused by capillary condensation of water at the mica surfaces as they are brought in close contact.

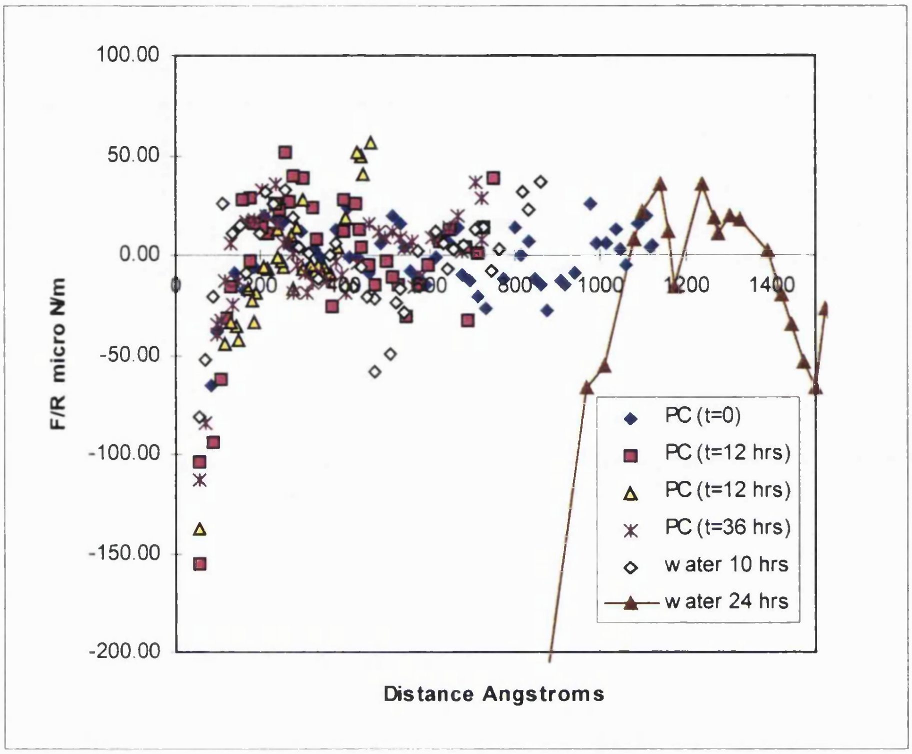


Figure 3.26 : Data from Figure 3.25 viewed using an expanded force scale

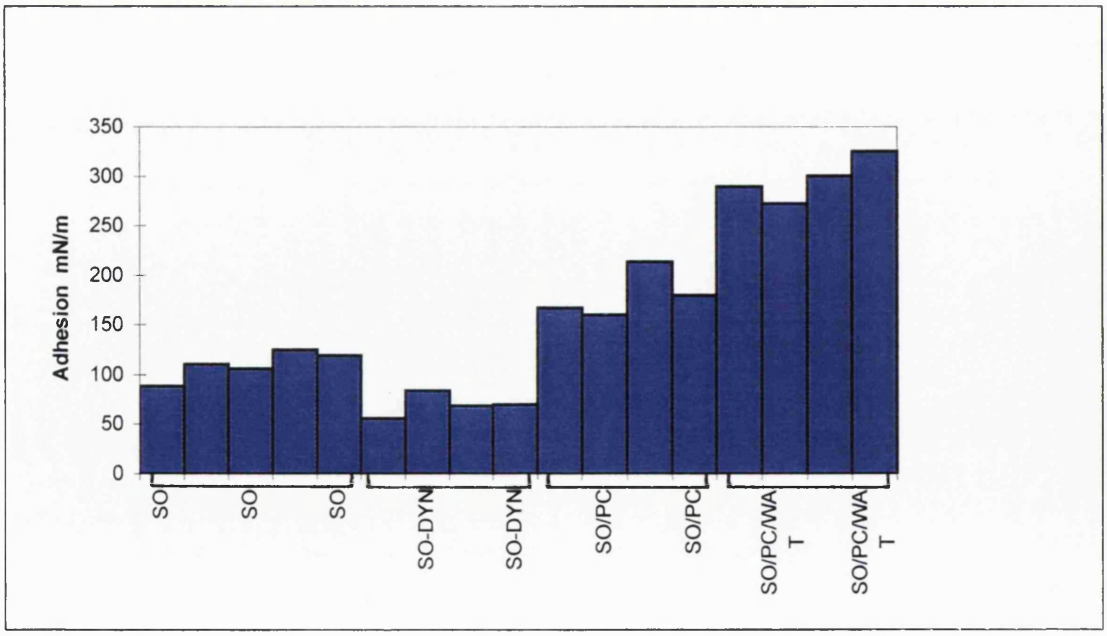


Figure 3.27 : Comparison of adhesion forces measured by pulling mica out of contact. SO= silicone fluid only, PC = propylene carbonate, DYN = expt carried out with one mica sheet vibrated at 1000 Hz and WAT = water.

Figure 3.27 shows a comparison of adhesive forces measured by pulling the mica sheets out of contact. Plotting the data in the form of a bar chart makes it clearer to see the differences in the force required to pull the mica sheets apart.

The following comments can be made :

- The lowest adhesion occurs with mica in contact with the dry silicone fluid (DC 1465). The value of approximately 100mN/m compares well with the pure OMCTS value of 50 mN/m obtained by Christenson and Blom (1986).

- Repeating the experiment using the oscillatory mode at an amplitude of a few hundred microns at 1000 Hz it is noted that there is a reduction in the adhesive force, by approximately 20 percent.

- Introducing the polar activators, propylene carbonate and water to the system had a significant effect on the adhesive force. Propylene carbonate required approximately twice the force to overcome the adhesive forces whereas the propylene carbonate and water mix required more than three times the amount. It should be noted that it is not possible to guarantee that both the propylene carbonate or silicone fluid was completely anhydrous despite efforts to dry the liquids, and that water may play the greater contribution to the forces required to separate the mica sheets.

Finally, the attempts to coat the mica with the quaternary ammonium compound proved to be unsuccessful. It was impossible to obtain a force distance curve. This was possibly due to the damage to the quaternary layer when re-separating the mica sheets after initial contact calibration was made. Despite numerous attempts to perfect the experiment, time did not allow further progression in this quest.

To summarise the findings:

- There appear to be no repulsion forces between bare mica sheets in silicone fluid.
- Silicone fluid DC1465 produces a rigid barrier to primary contact between molecularly smooth parallel mica sheets that are reported to be solvation forces.

- The periodic nature of solvation force is smoothed when solvent mixtures consist of molecules with different diameters.
- The presence of water appears to 'smooth' the solvation oscillations and causes a short-range depression in the force curve.
- The presence of water increases the adhesion energy between mica surfaces.
- Addition of propylene carbonate at activities less than 0.75 does not have any long range effects but is extremely important in determining the strength of adhesion between surfaces.

This study has provided information on the interaction of mica sheets that have not been coated with a quaternary ammonium compound as with Bentone 38. Therefore conclusions that can be drawn from this work must be done so cautiously. It has been assumed that on the scale of microns, montmorillonite clay and mica would behave in a similar fashion. However it should be reiterated that mica is distinct from other clay minerals in terms of surface charge density. SFM also does not account for the effects of platelet edges that could play a significant role in structuring. Finally this technique only displays the effects of surface forces between two interface pairs such that extrapolation to bulk rheological phenomena can only be made tentatively.

Despite this the studies performed using the mica sheets have provided a consistent pattern of results. The steep part of the theoretical part of the van der Waals attraction curve for OCMTS molecules is contained in what appears to be a strong solvation barrier i.e. the mica platelets cannot come into direct contact after initial separation. This would indicate that the polar activator and silicone fluids can accumulate on the surface of the mica sheets to build a second liquid phase. The propylene carbonate and water would appear to have no long range effects on attraction but do have a significant effect on adhesion. This is thought to be a result of polar activator condensing on the mica surface whereby a capillary mechanism arises that leads to an apparent attractive force at a distance that pulls the surfaces into adhesive contact from up to 0.1 micron.

3.7 Electrophoretic Studies

Electrophoresis is the steady translation of a particle under the influence of an external electric field. Electrophoretic mobility is widely used to measure the charge on small particles. Studies by early investigators found that practically every surface was charged when placed in an aqueous environment. These studies contributed greatly to the theory of electrokinetics by deriving relations between the velocity, the electrostatic potential at the surface and the applied field for thin double layers; these approaches are widely available in standard texts (Russel et al., 1995).

3.7.1 Background

Electrophoresis enables an understanding of the solid-solvent interface by providing information on the presence, sign and magnitude of its electrical charge. The study of solid-water interfaces have been widely investigated and characterised (Hunter, 1981). The characterisation of solid particles in non-aqueous media is much less well understood. This is due to the fact that firstly dissociation of electrolyte is far less significant than in aqueous media resulting in practical difficulties of identifying dissociation identities and concentrations of potential determining ions. Secondly, electrophoresis requires some knowledge of the physical dimensions of particles to provide information on the viscous drag coefficient, Debye length and ion concentration in order to relate particle mobility to the zeta potential.

3.7.2 Electrophoretic Experimental Work

3.7.2.1 Bentone 38 Gel Formulation

The gel suspension was prepared using Dow Corning Silicone fluid DC 1465 and Bentone 38.

The formulation used in this study was:

Bentone 38	6.7%
Silicone Fluid	93.3%

Polar activators were dosed in to the formulation as required. This is detailed in the experimental procedure.

3.7.2.2 Preparation of Organoclay Gel

Bentone 38 and Silicone fluid were blended together. This mixture was processed using the 2kg in-line Silverson Mixer rig using the method described earlier in this chapter. A total of five passes were made through the homogeniser to ensure thorough mixing. The mixture was then passed twice through a high-pressure homogeniser (APV Rannie Minilab) set at 1000 bar. A bulk quantity of gel was prepared (1kg) for the test for shipping to the University of Minnesota, US where the experiments were to be performed.

3.7.2.3 Electrophoretic Light Scattering Methodology

The electrophoretic mobility of clay particles suspended in silicone fluid with various polar activators was measured using custom built Electrophoretic Light Scattering Apparatus (ELS). This is located at the Centre for Interfacial Engineering, University of Minnesota and Peter Carew (Unilever Research Port Sunlight) kindly assisted with the experiments.

The green component from an Argon ion laser was used as the source and the particle velocities in the ELS cell were measured with a standard optical train (TSI, St. Paul, MN, USA). Two beams crossing at an angle of 21.48° in the air made up the dual beam geometry. A schematic of the cell is shown in Figure 3.28.

One of the laser beams was frequency shifted by 50 kHz with respect of the other. This arrangement allows for determination of the signs of the charges of the particle surface once an electric field is in force. The desired electric field was generated by amplifying a voltage output from a PC based Data Acquisition board. To avoid electrode polarisation and reduce space charge effects, the electric field was applied for limited periods only (4ms–2s) depending on the actual field strength and then reversed for the same period. Shorter field on-times were required for higher field strengths. Shorter pulses decrease the precision of the measured mobility value by reducing the frequency resolution of the acquired spectrum of mobilities. Thus for a given field strength, the field on-time was varied until an optimum was found i.e. when the result for the on-time and half of the on-time were concordant.

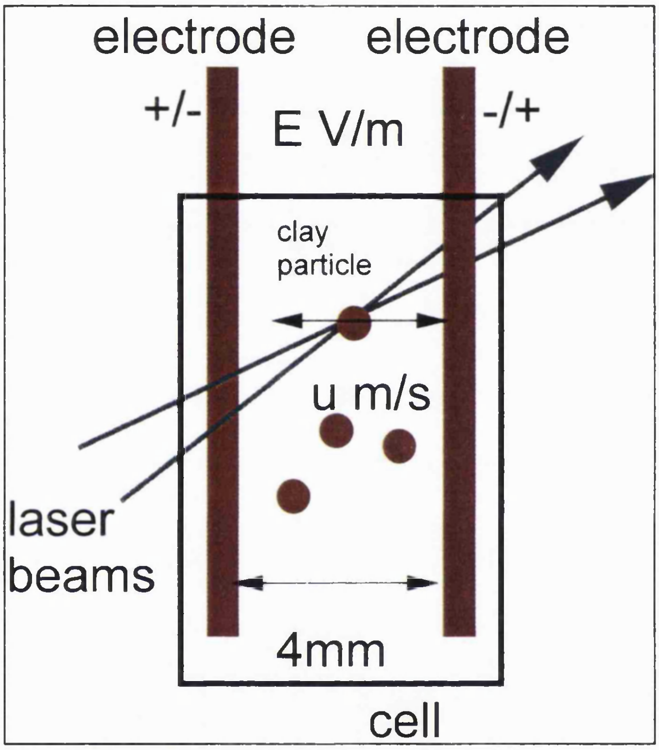


Figure 3.28 : Schematic diagram of the ELS electrodes and cell

For the clay/silicone fluid systems, mobility was found to be dependent upon the field strength, which for electrodes separated by a distance of 4mm, mobility could be as high as 5000 V/cm. The mobility, was therefore, measured for a range of fields (250-5000 V/cm) and was found to be repeatable when the sample preparation protocol was followed.

3.7.2.4 Electrophoretic Light Scattering Sample Preparation

ELS combines high strength, rapidly fluctuating electrical fields with Laser Doppler Anemometry (LDA) for partial velocimetry (Parfitt and Peacock 1969; Jin et al, 1998).

To ensure repeatable, relatively noise free particle distributions are obtained, samples must be of relatively low concentration and therefore it was necessary to dilute the clay suspensions.

To create suitable dispersions of organoclay, a large number of tests were carried out before a suitable sample preparation was finalised which is detailed as follows:

1. Prepared Bentone gel (0.1g) was dispersed into silicone fluid* (20ml) and shaken vigorously by hand to break up the gel. The mixture was sonicated for 30 minutes.
2. To produce the sample for the ELS experiment, 0.4ml of this dispersion was diluted into a further 3ml of silicone fluid*.
3. The spectrometer cuvette was charged with approximately half of this dispersion.
4. The cuvette was earthed with aluminium foil to prevent static build up.

* The silicone fluid used for dilution was stored over a 4 Angstrom sieve for one week and filtered (0.2μm) before use.

Assuming total absence of flocculation and a particle size of 1μm, the final clay interparticle distance was estimated to be of the order of 40μm when full dispersion was assumed.

It was however noted that after a few minutes, flocs appeared to form and therefore it was necessary to shake the entire cell vigorously at fixed intervals, which appeared to disperse the flocs.

To examine the effects of polar activator, two methods were used. For immiscible activators, the clay gel dispersion was diluted using silicone fluid that had been stored in equilibrium with activator. For example, dry silicone was stored over propylene carbonate. For activators that were miscible with silicone fluid, a 10%w/w solution of the activator was used. The concentration used was completely arbitrary since the concentration of immiscible polar activator (propylene carbonate) in silicone fluid was unknown. The aim was to ensure an excess of activator in all cases.

The activators tested were:

- propylene carbonate
- methanol
- water
- acetone
- methyl ethyl ketone
- ethanol
- cyclohexane
- cyclohexanol
- cyclohexanone

Of the polar activators tested, only propylene carbonate, methanol and water were substantially immiscible with silicone fluid.

The effect of increasing the activity of propylene carbonate on the particle charge of Bentone 38 was carried out by diluting the gel with the silicone fluid saturated with propylene carbonate which was itself diluted to produce activities of 1.0 (saturated), 0.5, 0.25 and 0.125.

3.8 Electrophoretic Results

3.8.1 Particle Mobility over a Range of Electric Field Strengths

Mobility spectra may be obtained by measuring the velocity of many particles over many cycles. The measure of intensity is a relative value for the signal from the photomultiplier for a given sample. From this, the average mobility may be approximated.

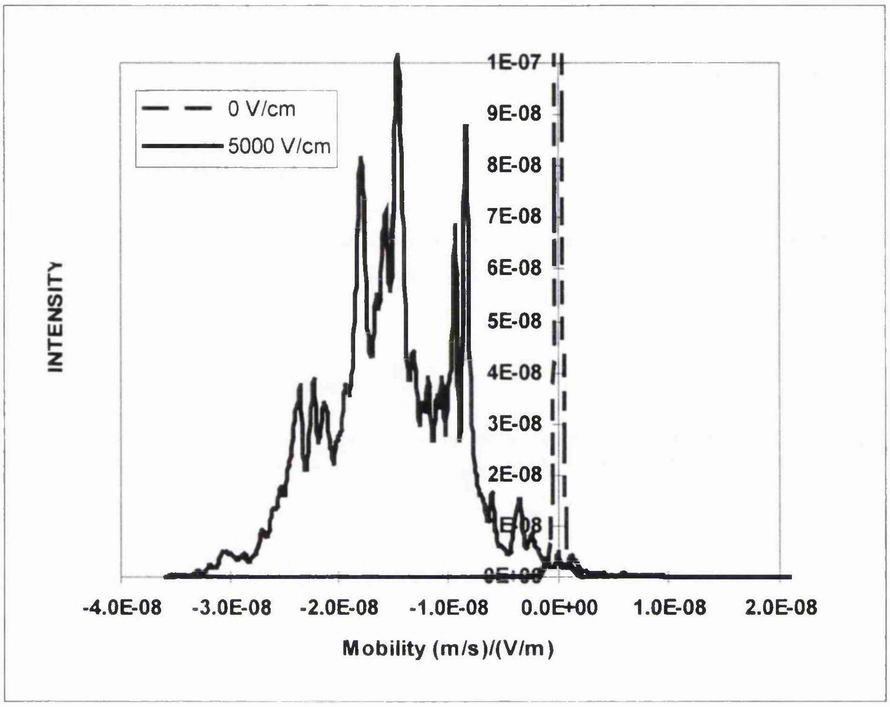


Figure 3.29 : Typical electrophoretic mobility data.
Clay/Silicone fluid dispersion with 10% acetone added.

Figure 3.29 shows an example of typical electrophoretic mobility data for acetone. Further results are provided in Appendix 3.1. Mobility data was gathered for each sample over a range of fields. The samples were deemed reproducible when the mean mobilities calculated from the spectra were within 10% of each other.

For the sample that was activated with acetone, a negative shift is shown that indicates the majority of particles are negatively charged. The average mobility is approximately -1.75×10^{-8} (m/s)/(V/m). Each clay/silicone fluid dispersion was tested using different polar activators over a range of field strengths. The mean mobility for each data set was then calculated and then plotted. These data are displayed in Figure 3.30

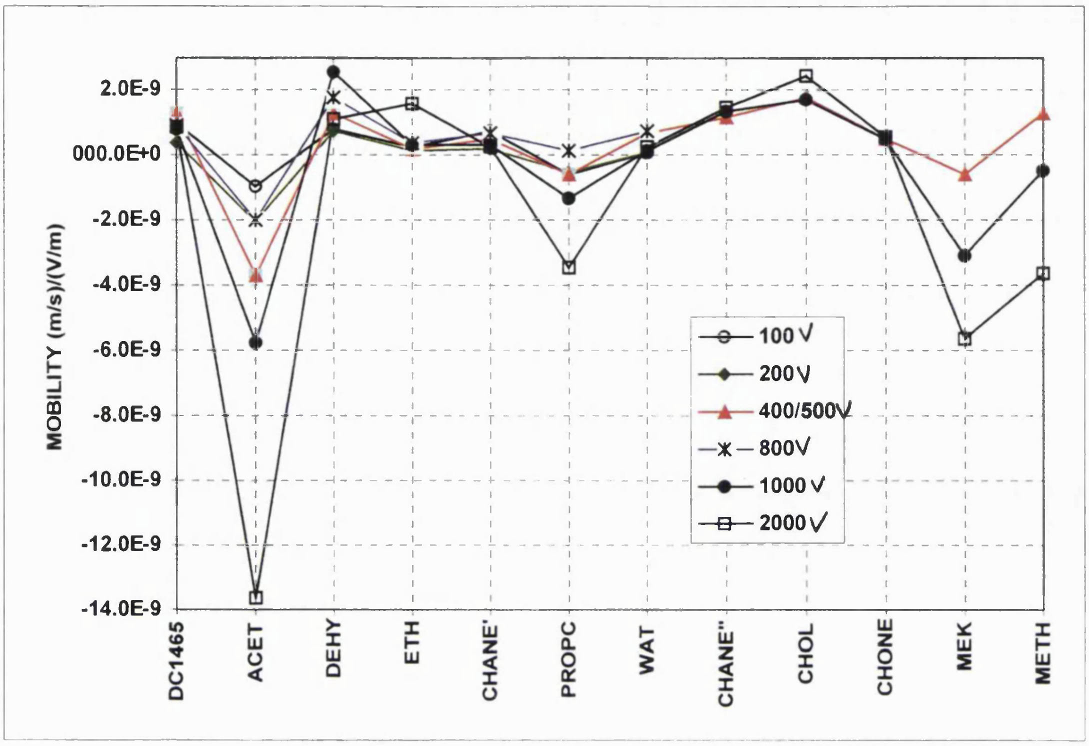


Figure 3.30 : Mean mobility values at different electrode voltages (divide by 0.4 to retrieve field strength in V/cm) for different activators.

DC1465=silicone fluid oil raw material, ACET=acetone, DEHY=dehydrated DC1465, ETH=ethanol, CHANE'=first cyclohexane test, PROPC=propylene carbonate, WAT=water, CHANE"=second cyclohexane test, CHOL=cyclohexanol, CHONE=cyclohexanone, MEK=methyl ethyl ketone, METH=methanol.

The following trends may be drawn:

- Positive mobility is recorded for all the silicone test fluids (Dehydrated DC 1465, raw DC1465 and DC1465 saturated with water. The mobility of the particles is very small regardless of field strength.
- The samples prepared with cyclohexane displayed slightly positive mobility. These results were to be expected to be similar to those of the dehydrated and raw silicone fluid samples due to the non-polar nature of the additive.
- Acetone, Propylene Carbonate and Methyl Ethyl Ketone all produce negative particles that are significantly influenced by field strength.

- Methanol produces particles that appear to be negative at high voltages and positive at low voltages.
- Increasing voltage produces an increase in apparent mobility in the same direction as polarity (see Figure 3.31 for expanded axis for finer detail)
- Polar additives yielding negative charges, each of which carries a carbonyl group, produces mobilities with the greatest magnitudes.
- The cyclic species cyclohexane, cyclohexanol and cyclohexanone all produce positive charges. N.B. Cyclohexanone, which carries a carbonyl group does not produce a negative shift.
- The additives that produce the greatest negative shift (acetone, propylene carbonate and methyl ethyl ketone) display the greatest sensitivity to voltage which suggests an affinity to surface interaction with these molecules.

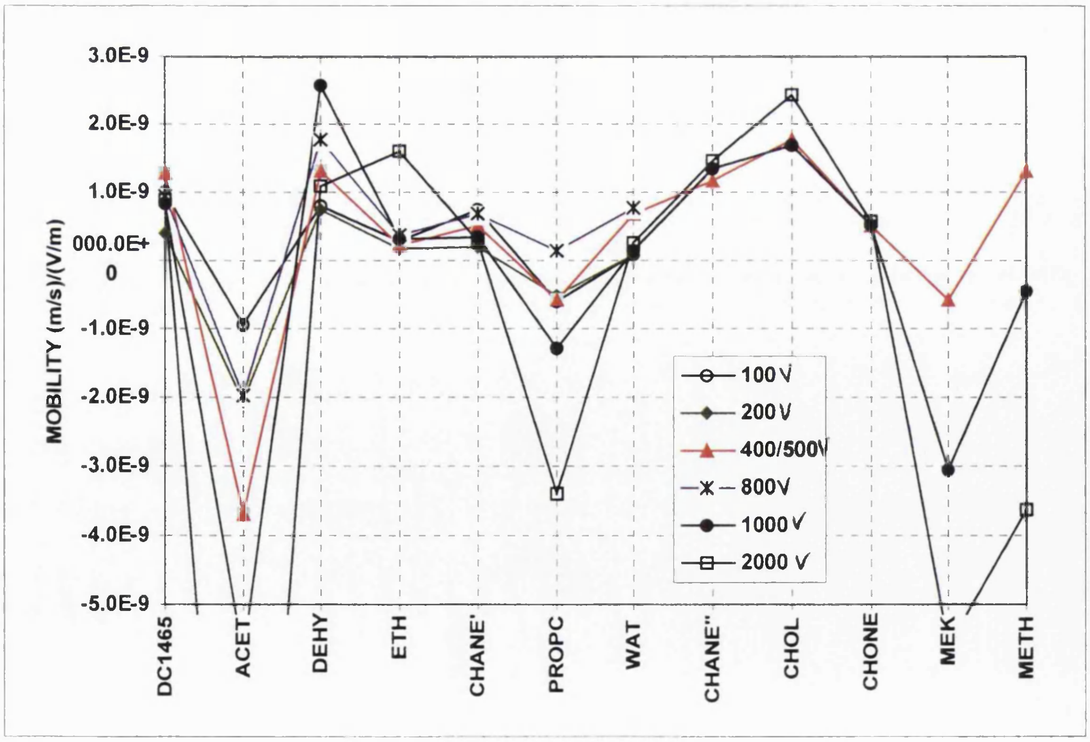


Figure 3.31 : Mean mobility values of polar activators at different electrode values (graph as Figure 3.30, replotted on expanded axis)

3.8.2 Electrophoretic Mobility with Differing Propylene Carbonate Activity

From the previous data, it is clear to see that trace quantities of propylene carbonate dissolved in the silicone fluid used to dilute the gel was sufficient to yield a negative charge on the particles. The 'saturated' sample was diluted to show the effect of starving the clay particles of propylene carbonate on particle mobility. Figure 3.32 shows the effect of propylene carbonate activity on particle mobility at 500 V (1250 V/cm).

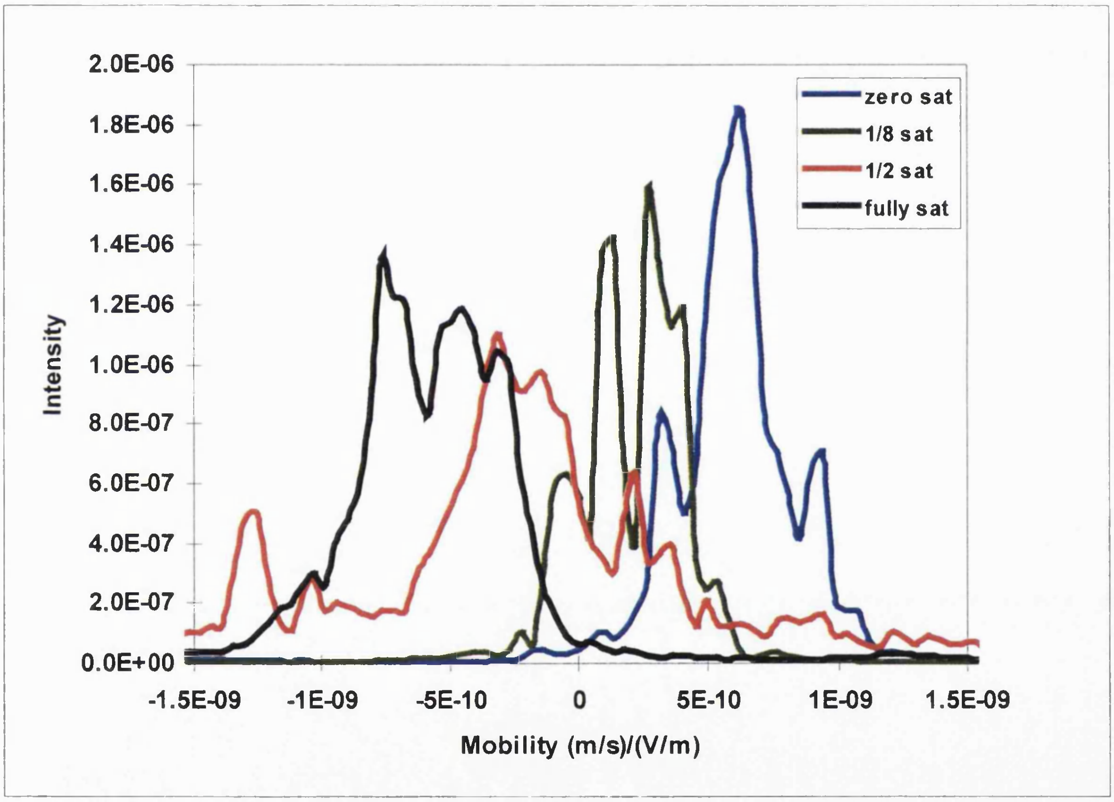


Figure 3.32 : Sensitivity of electrophoretic mobility spectra to propylene carbonate activity.

The following trends are observed:

- The bulk of particles that appear to be negatively charged are so, when saturation is greater than 0.5.
- At zero saturation, almost all particles appear to be positively charged whereas at complete saturation particles a primarily positive.

- At intermediate saturation, the spectra spans between positive and negatively charged particles.

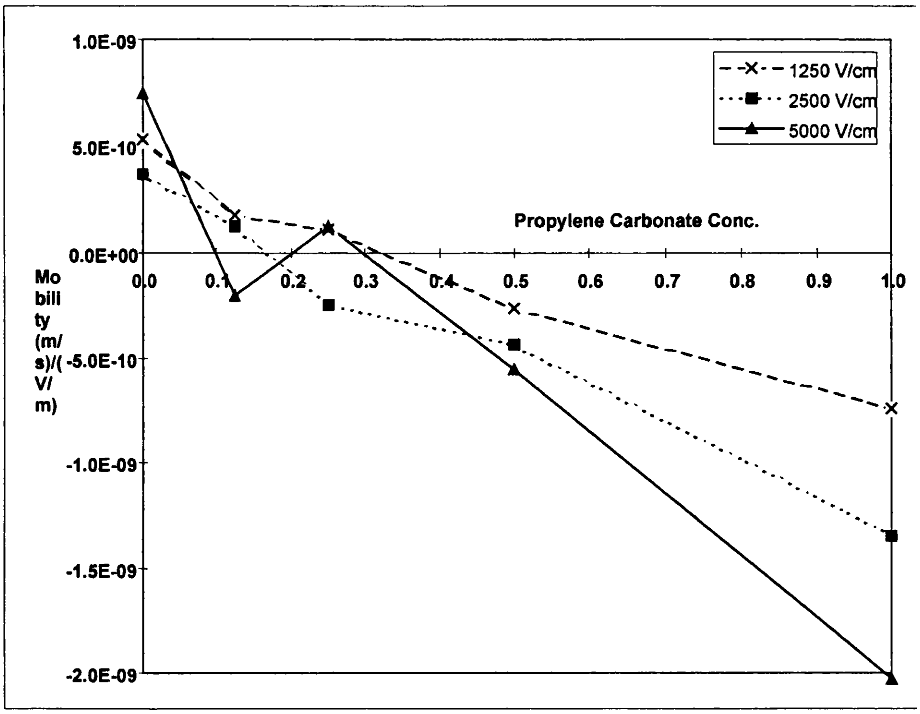


Figure 3.33 : Variation of mean mobility of organoclay particles with propylene carbonate saturation concentration and field strength

Figure 3.33 shows the trend in mean mobility value at varying field strengths across the range of propylene carbonate saturation. (N.B. 1.0 denotes fully saturated) It is clear from this data that:

- At zero saturation, the clay particles are positively charged.
- The point at which the mean charge is zero is difficult to identify and probably lies between 0.125 and 0.25 saturation.
- At 0.5 saturation, the particles are clearly negative and mobility increases linearly with increased field strength.
- At full saturation, the mobility is approximately double the value for 0.5 saturation.

- The dependence of mobility on field strength is approximately equal for all saturation levels less than or equal to 0.5 however, at full saturation (1.0), there is a significant difference between the mobility value at 1250 V/cm and that of 5000 V/cm.

3.9 Summary

This chapter has focused upon the interaction of polar activators and clay. A review of swelling and sedimentation of Bentone 38 and silicone fluid was made with a range of polar activators. These included polar activators that are commercially available and recommended by Bentone 38 suppliers as well as a number selected from a list of recommended polar activators. This selection was based on the effectiveness ranking and the functional group associated with the molecule.

Surface force measurements were carried out using a model clay (Mica) to determine the interaction of silicone fluid and polar molecules with the surface of mica sheets. Attempts to coat the Mica clay with the quaternary ammonium compound to correlate the results to Bentone 38 however this proved to be unsuccessful. Nevertheless an insight into the understanding of the affinity polar activators have to clay surfaces has been made. Preliminary investigations into the forces of attraction that exist between platelets in non-aqueous fluid have also been established.

The final section of polar activator study focused on the electrophoretic mobility of polar activators. Here a range of polar activators was selected to determine the mobility of polar molecules and the effect they have on the net charge of Bentone 38 clay.

CHAPTER FOUR

THE EFFECTS OF PROCESSING THROUGH MECHANICAL AND THERMAL ENERGY

4.1 Processing Effects on the Structuring of Bentone 38 Gels

4.1.1 Forward to Experiments

It has been shown from the previous experiments that polar activators contribute to the swelling of Bentone 38 platelets in a non-polar solvent. The optimum polar activator investigated (propylene carbonate), as an entity, did not provide sufficient swelling capabilities to overcome the short range forces of attraction (van der Waals) to enable dispersion and therefore gelation and a second force is required. The process methodology for structuring Bentone 38 is key to creating a gel, however, as reviewed in the literature in Chapter One, very limited studies have been made in this area as to the effects of different processing regimes. The processing methodology is somewhat nebulous and therefore the following experiments will attempt to determine the effect of thermal energy and mechanical energy on dispersion of clay platelets and endeavour to quantify the minimum requirements to achieve the transformation of a mixture that sediments rapidly to a stable gel. To complement this, an attempt to gain a better understanding of the microstructure of the gelled network will be made.

4.2 The Effect of Mechanical Shear

4.2.1 Experimental Processing Equipment

To determine the effect of mechanical energy on dispersion/gelation it was necessary to review a range of shear devices. To consider the effect of mechanical energy on deagglomeration, it is worth considering what is physically happening. Bentone 38, as has been previously explained, is composed of agglomerates of particles held together by attractive forces. Adding a polar activator that encourages platelet swelling, and then forcing these agglomerates through a narrow gap under a turbulent regime, in theory, would break up the agglomerates to smaller dimension since the mechanical forces would be significant to overcome the van der Waals attractions. If this were true, the question that then must be considered is whether a swelling agent is required and is it possible to provide enough energy by means of mechanical methods. In order to be able to qualify this, it is necessary to have a picture of the microstructure of the Bentone 38 and therefore visualisation techniques (e.g. optical) are critical.

4.2.2 Types of Shear Applied

There is a wide range of shear devices available commercially and it would not be feasible to evaluate each and every one. A number of different devices were selected for evaluation that enabled a wide range of shear rates to be examined from low shear mixing to excessively high shear (high pressure homogenisation).

4.2.2.1 Low Shear (Heidolph Stirrer)

The Heidolph stirrer (Heidolph-Electro, Germany) consists of a variable speed electric motor (45 – 2000 rpm) mounted on a heavy base stand. An impeller stirrer (paddle) was used (tip speed = 0.7 m/s @ 200 rpm; 1.4 m/s @ 400 rpm). The Heidolph stirrer provides laminar flow.

4.2.2.2 Medium Shear (Laboratory Scale Silverson L4R Homogeniser)

The Silverson L4R Homogeniser is a standard laboratory propriety mixer. It is supplied by Silverson Machines Ltd, UK and is primarily used for droplet breakdown in emulsions. It can be used as a stand-alone mixer where the shear element is immersed into a vessel containing the medium to be sheared, or a bespoke in-line head may be fitted. In either mode, the shear elements are of the same configuration. The rotor is driven by a variable speed motor (up to 9,900 rpm) and can reach a tip speed of 16 m/s. This combined with a rotor-stator gap of order 0.27 mm leads to gap shear rates in the order of 60,000 s^{-1}. The Silverson Homogeniser may provide laminar, transitional or turbulent shear depending upon the Reynolds Number (R*e*) and Power number (P*o*) of the mixture being sheared. This will be discussed in greater detail in Chapter Six. (Edwards et al, 2000)

4.2.2.3 Medium Shear (Pilot Scale Silverson Homogeniser)

The pilot scale homogeniser (Silverson) is connected via a recirculation loop to a 30kg vessel (see Figure 2.4). An in-line lobe pump (APV) maintains flow. The homogeniser consists of two standard emulsor (square holed) screens and a series of rotor blades connected to a drive shaft. The rotor is driven by a 3kW variable speed motor (0-100%, max speed 5000 rpm) and reaches a tip speed of 16.76 m/s. The rotor-stator gap is of the order of 0.4 mm which enables a maximum shear rate of 41,000 s^{-1}.

4.2.2.4 High Shear (Sonolator)

The Sonolator is an in-line homogeniser designed to convert the kinetic energy of a high velocity liquid stream into intense mixing energy. Process liquid is forced through an elliptical orifice at a rate of 300 ft/s using a positive displacement pump. Within the path of the stream is a blade like obstacle. As the mixture exits the orifice and approaches the blade, perpendicular vortices are generated that causes ultrasonic oscillation within the liquid. The stresses set up within the fluid by these oscillations cause the fluid to cavitate. It is said that the high level of cavitation, shear and turbulence within the Sonolator mixing chamber is responsible for de-agglomerating particles.

4.2.2.5 Very High Shear Rate (High Pressure Rannie Homogeniser)

The high pressure Rannie Homogeniser (Minilab, type 7.30 VH) consists of a high-pressure displacement pump. The operation is such that product is fed into the homogenisation block where two pistons work in sequence forcing the test material radially through a ceramic homogenisation valve that is adjusted manually by means of a hand operated screw. As pressure is increased, the gap becomes narrower and thus increases shear rate.

It is difficult to accurately measure the shear rate of the high-pressure homogeniser on account of the practicalities of measuring the gap size and the variability of parameters such as flow velocity that is perceived to be considerably higher through the gap than the mean flow velocity measured. Using typical values quoted for a commercial high-pressure homogeniser with a mean flow velocity of $50ms^{-1}$ and a gap between 15-300μm it is possible to say that the shear rate is in the region of $(0.1 - 3.3) \times 10^6 s^{-1}$. (Dickinson, 1994).

The flow through a high pressure Rannie is often described as extensional flow. This can be likened to the dragging of a droplet in a lateral direction so that it extends in one plane to a point where it will split into two discrete particles.

4.2.2.6 Very High Shear (APV Lab 2000 Homogeniser)

A second High Pressure Homogeniser was also used due to technical failure of the Minilab during the experimental progress. The Rannie Lab 2000 replaces the Minilab homogeniser as a commercially interchangeable item. The key difference in the two models is that the product is gravity fed via a funnel into the mixing chamber where one piston only pumps the test fluid through the homogenisation valve. The pressure range and dimensions of the valve are equivalent to the Minilab model. A description of the valve assembly and images can be found in Appendix 4.1.

4.3 Mechanical Energy Experiments

4.3.1 The Effect of Low Shear Rate Mixing

Suspensions of Bentone 38 were prepared with and without propylene carbonate using the formulation specified in Chapter 2. The suspensions were stirred in a vessel using a

Heidolph stirrer (200 rpm and 400 rpm). The viscosity of the suspension was measured using a Brookfield Helipath viscometer at intervals over a period of 30 minutes.

4.3.2 The Effect of Medium Shear Mixing

4.3.2.1 Laboratory Scale (2 kg)

Using the same formulations, the suspensions were then processed through the in-line L4R Silverson homogeniser. Samples were taken after each pass through the homogeniser for viscosity measurement. A total of ten passes was completed. Finally, each test formulation was subjected to a period of ten minutes shearing using the dip-in L4R Silverson homogeniser and the In-line L4R Silverson homogeniser. The In-line Rig was set up in a re-circulation mode by placing the return hose back into the feeding vessel.

4.3.2.2 Pilot Plant Scale (30kg)

The effect of scale up was also investigated. 30kg batches of each formulation were processed on the 30 kg Universal Mixer (see Figure 2.5). The mixer was set up in recirculation mode with the following parameters:

▪ Impeller speed	100rpm
▪ Pump Speed	150 rpm
▪ Silverson	maximum speed (100% setting)
▪ Temperature	25°C or 50°C

The suspensions were recirculated in the vessel for a period of 30 minutes. Samples for optical microscopy and viscosity were taken at intervals over a period of 30 minutes.

4.3.2.3 The Effect of High Shear Mixing

Batches of each formulation were prepared and processed through the sonolator with repeated passes until it was no longer possible to maintain a flow. Pressures were maintained in the region of 3000-4000 psi for each run.

4.3.2.4 The Effect of Very High Shear Mixing

A pre-mix of each test suspension was prepared using the in-line Silverson Homogeniser (5 passes) to ensure the clay was wetted and any large agglomerates had been dispersed. Each premix was passed through APV Rannie Homogeniser (Minilab and 2000 models) over a series of passes and at variable pressures. Initial trials were run on the APV Minilab and a more comprehensive study was completed using the APV 2000 Rannie Homogeniser.

4.4 Thermal Energy Experiments

4.4.1 Forward

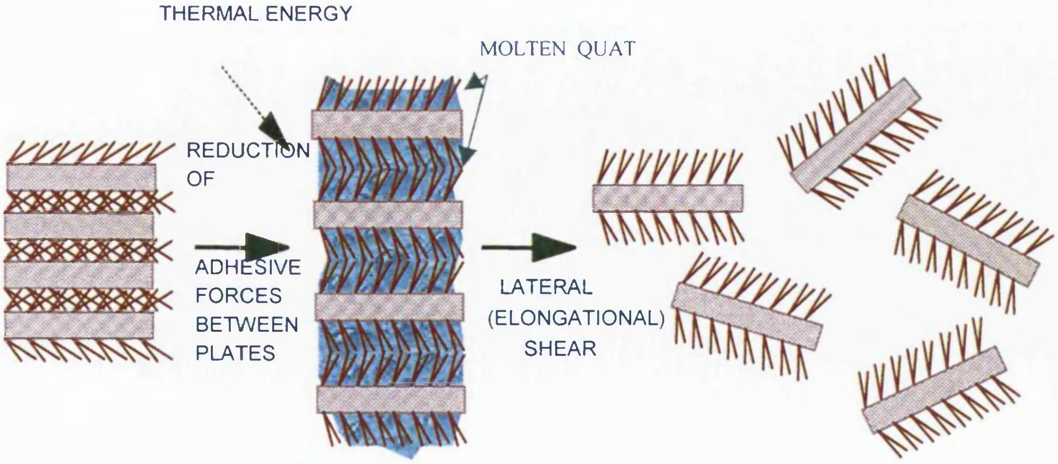


Figure 4.1 : Schematic of the process of delamination of clay platelets through lateral shear and elevated temperature processing

The following experiments were to determine the effect of heat primarily on Bentone 38 and secondly whether it was beneficial in processing. The theory behind investigating the effect of temperature lies in the physical properties of the quaternary ammonium compound on the surface of the clay that is semi-solid at room temperature and is denoted as the L_β phase. It has a rigid format due to local ordering of carbon chains. It is thought that if the temperature were raised so as to cause a phase transition to the liquid L_α phase, the molecules of the quaternary compound would be free to diffuse. In a liquid form the attractive forces would be significantly lower and therefore delamination should be easier to achieve through lateral shear or extensional flow. A diagram of the procedure for delamination is shown in Figure 4.1.

4.5 Determination of Phase Transition

4.5.1 Differential Scanning Calorimetry

The first stage was to determine whether a phase transition was observed in the heating and cooling cycle of Bentone 38 that was within a practical processing range (<100°C).

Initially conventional Differential Scanning Calorimetry was tested using a sample of Bentone 38. Unhydrophobed Bentone 38 was used as a reference. The unhydrophobed sample of Bentone 38 was prepared in the Measurement Science Unit, Unilever Research using a standard extraction technique using a Soxhlet extraction unit. The method for quaternary extraction can be found in Appendix 4.2

4.5.2 High Sensitivity Differential Scanning Calorimetry

Further experiments were performed using a High Sensitivity Differential Scanning Calorimeter (HSDSC) (Micro DSC III, Setaram, London School of Pharmacy, University of London). This techniques determines the variation of heat flow given out or taken in by a sample when it undergoes temperature scanning in a controlled atmosphere. The advantage of HSDSC is that it enables solutions to be evaluated where conventional DSC is not sensitive enough. It also enables determination of very small volumes of materials undergoing phase transitions. Since the quantity of quaternary ammonium on the surface of Bentone 38 is a significantly lower ratio to the clay itself, this technique proved to be highly useful in determining phase transitions.

4.5.3 HSDSC Sample Preparation

Samples of test mixtures and their references were weighed highly accurately using a four figure balance into precision engineered cells. The cells required a highly rigorous cleaning and drying regime to ensure no debris would contaminate the results. The cells were handled only when wearing latex gloves to prevent any cross contamination from the skin.

Between approximately 500 mg and 800 mg were weighed into each cell. The lids were tightened with a spanner. An o-ring was used for each cell to ensure a good seal was achieved and that volatile materials could not escape.The cells were inserted into the calorimetric block, which is composed of a gold cylinder. Gold cylinders were placed over the cells to minimise temperature fluctuations throughout the experimental period.

The experimental parameters used for the experiments were as follows:

▪ Temperature sequence	20 – 55°C
▪ Temperature ramp	1K/min
▪ Sequence	heat cycle and cool cycle

The samples investigated were as follows:

Sample	**Reference**
Bentone 38/Silicone Fluid/Prop.Carb	Silicone Fluid/Propylene Carbonate
Bentone 38/Silicone Fluid	Silicone Fluid
Bentone 38	Unhydrophobed Bentone 38
Silicone/Propylene Carbonate	Silicone Fluid
Bentone 38/SiliconeFluid/Ethanol	Silicone Fluid/Ethanol
Bentone 38/Silicone Fluid/Hexane	Silicone Fluid/Hexane

4.6 The Effect of Temperature on Processing Bentone 38

Using the information obtained from HSDSC it was possible to identify that the quaternary ammonium compound on Bentone 38 exhibited a phase transition over a distinct temperature range. Having established this phase transition for Bentone 38 dry and in the presence of solvent and polar activator that was reliably reproducible, the next phase was to establish whether processing at elevated temperature had a significant effect on the delamination and creation of a stable gel network.

4.6.1 Low Shear Rate Mixing

A water bath was heated to 50°C and maintained at this temperature. A mixture of Bentone 38 and Silicone Fluid 1465 was allowed to come to equilibrium. The temperature of the clay mix was measured using a temperature probe. The clay suspension was stirred using a paddle stirrer (200 rpm, 5 minutes).

4.6.2 Medium Shear Rate Mixing

Bentone 38 and Silicone Fluid were shear mixed using the in-line Silverson L4R mixer and the pilot plant scale double screen homogeniser.

For the experiment using the laboratory scale homogeniser, a total of 5 in-line passes were performed. The feed vessel and return vessel were positioned in a water bath set at 50°C for the duration of the experiment and the mixture allowed to reach equilibrium prior to commencing shearing.

The pilot plant scale experiments were carried out on the 30kg Universal Mixer. The jacket temperature of the vessel was set to 52°C and the mixture recirculated through the vessel recirculation loop. An in-line temperature probe in the recirculation loop allows for accurate measurement of the product temperature. The temperature of the jacket was adjusted until the product temperature had reached a stable 50°C. At this point, the double screen Silverson homogeniser was switched on and the product was sheared for a total of thirty minutes.

4.6.3 Very High Shear Mixing

To maintain the temperature through the APV Rannie homogeniser is somewhat difficult since there is no water jacket to maintain constant temperature. The mixture of Bentone 38 and Silicone Fluid was heated in a water bath to 50°C and transferred to the feed funnel of the homogeniser. The mixture was immediately processed through the homogeniser to reduce temperature loss through cooling. The temperature of the product was measured as a precaution to ensure temperature had not fallen below that of the test temperature. It was noted that after the initial pass and a second pass that the final temperatures were 55°C and 58°C respectively.

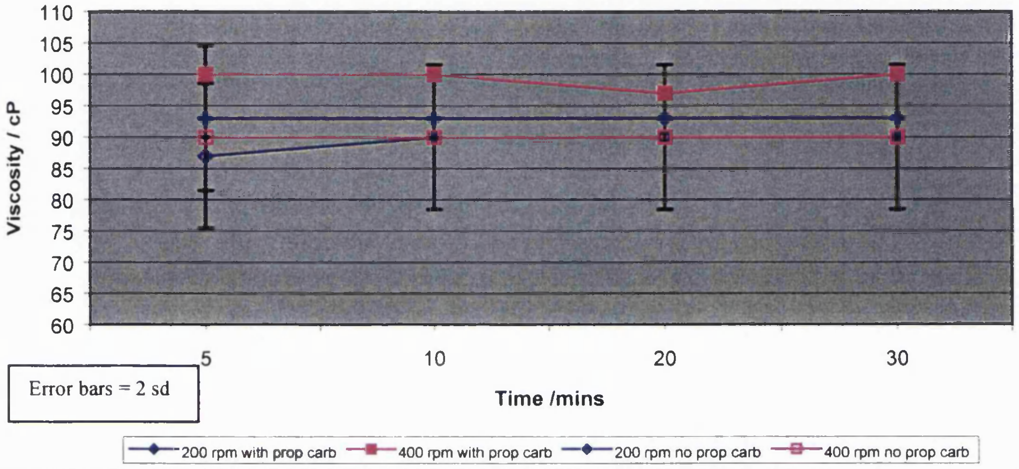
It should be noted that propylene carbonate was not included in this study with the exception of the pilot plant scale experiments where the process was repeated with polar activator. The reason was to establish the individual effect temperature had on the structuring of Bentone 38 clay.

4.7 Results

4.7.1 The Effect of Low Shear Rate Mixing

Graph 4.2 represents the mean results of low shear mixing over time of organoclay and silicone, with and without the polar activator, propylene carbonate. It is evident from the data plotted in the graph that low shear rate has no significant effect on product viscosity with time regardless of whether propylene carbonate is present. It can be noted that in the presence of propylene carbonate, there is a very slight increase in viscosity but can not be deemed as significant. This is most likely attributed to the swelling of Bentone 38 with polar activator causing a slight increase in particle dimensions and therefore increasing the volume phase of the solid matter in the formulation. It can be concluded that low shear stirring cannot overcome the attractive forces between Bentone 38 platelets and therefore delamination and gelation cannot be achieved through the mechanics of this process.

Figure 4.2 : Graph to show the effect on base viscosity of Bentone/Silicone Mix (with and without Propylene carbonate) over time at different stirring speeds using a heidolph stirrer, n=3



Error bars = 2 sd

4.7.2 The Effect of Medium Shear Rate Mixing

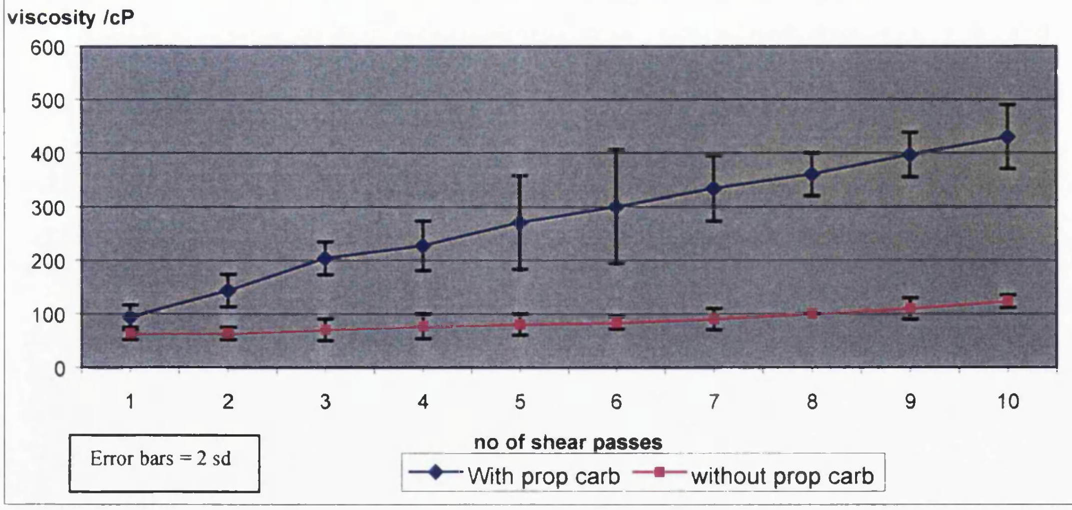
When the same formulations are subjected to an increase in shear rate through a laboratory scale Silverson L4R homogeniser, the increase in product viscosity (as shown in Figure 4.3) is more apparent than the viscosities after low shear mixing that were shown in the graph of Figure 4.2. The graph represents the mean data for a series of experiments that compared the effect of increasing the number of shear passes through an in-line homogeniser against bulk viscosity. This experiment enabled confidence that all the agglomerates in the formulations experienced the same quantitative amount of shear since a constant flow rate from one vessel to another via the homogeniser was maintained throughout.

The following comments can be made:

- The most notable feature of the results in the graph is that propylene carbonate plays a significant role in the build of viscosity over the number of shear passes. For the system that has no polar activator present, viscosity builds very gradually with increased shear passes with viscosity being double after ten passes.

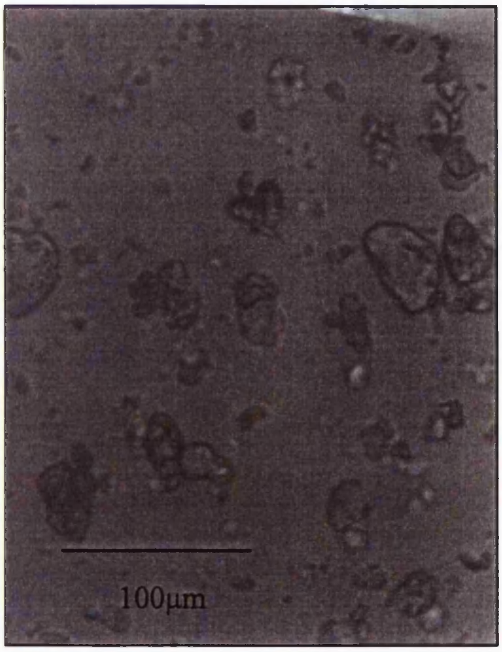
- Conversely, when propylene carbonate is present in the formulation, viscosity is seen to be directly proportional to the number of shear passes. The cumulative effect of shear passes causes the viscosity to increase over four times its original value. This is possibly due to the increase in intrinsic mixing of propylene carbonate molecules and the accessibility to intercalation of platelets causing better swelling and delamination through increased shear.

Figure 4.3 : Graph to show the effect of the number of shear passes through an in-line Silverson homogeniser on viscosity, n=3



It should however be commented on at this stage that a physical appearance of the mixture was not that of a gel or semi-solid but would be described as a viscous liquid. The medium was prone to syneresis seen by gross leakage of silicone fluid layering at the top of the samples taken. This would indicate that the structure of the viscous liquid was composed of a number of agglomerates that, with time were subject to compaction through gravity. The gravitation force outweighs the weak forces that bind a structure together causing the larger particles to compact and result in silicone fluid to be compressed out of the structure and form a layer on the upper surface of the sample.

Optical microscopy images shown in Figures 4.4 and 4.5, indeed show the presence of large agglomerates to support this and concludes that homogenisation, even with cumulative shear passes does not provide sufficient energy to fully delaminate clay primary particles. It can be seen in both micrographs that the distribution of particles is polydisperse with particles ranging in size from less than ten microns to agglomerate dimensions in the region of 40 to 50 µm diameter. The micrograph of Figure 4.5 would indicate that a certain degree of dispersion of agglomerates has occurred since there is a greater number of smaller sized agglomerates present. These smaller agglomerates are representative of the weak structure that has been built through the action of propylene carbonate aiding delamination. However, the Silverson homogeniser does not apparently provide adequate shear to fully delaminate clay particles.



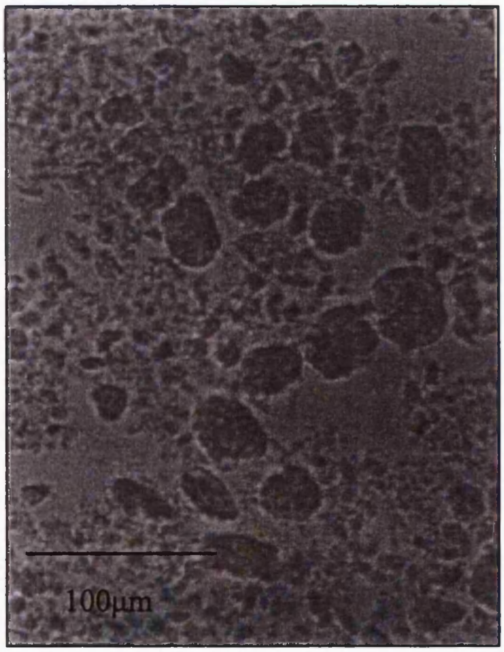


Figure 4.4 (left) : Micrograph of Bentone + Silicone sample 10 pass through homogeniser (x20 DIC)
Figure 4.5 (right) : Micrograph of Bentone + Silicone + Prop Carb sample 10 pass through homogeniser (x20 DIC)

4.7.3 A Comparison Between Low and Medium Shear Mixing

To compare different shear devices keeping time as a constant factor is shown in Figure 4.6. Once again, the significant effect of the polar activator propylene carbonate is highlighted. This is only significant, however, for the formulations processed using the Silverson homogenisers. In the absence of polar activator, the viscosities of all samples are independent of shear rate. The difference between the viscosities produced using the two Silversons is attributed to the amount of time the formulation sees the homogeniser head. The in-line homogeniser had a flow rate of ~24l/hr that in a ten minute period would equate to four batch cycles. This means that using a recirculation process through an in-line Silverson homogeniser, an agglomerate would only see shear four times in ten minutes.

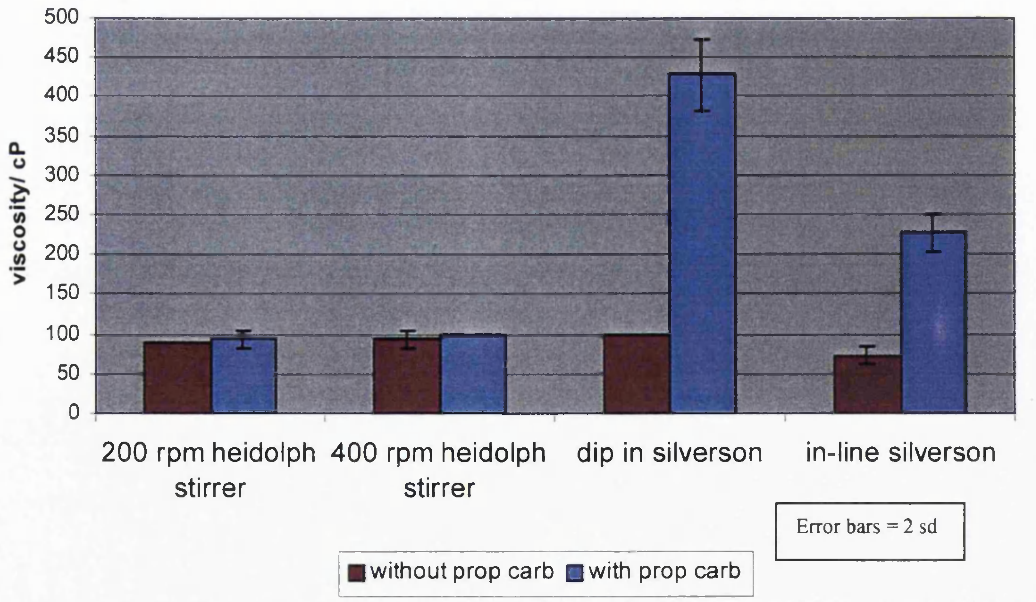


Figure 4.6 : Graph to show Brookfield Viscosity measurements (TA @10rpm) after shear (10 min) with different shear devises

Referring back to Figure 4.3, the viscosity reading after four passes was equivalent to the viscosity measured for ten minutes recirculation. The viscosity measurement for the batch process using the dip-in Silverson homogeniser gave a significantly higher bulk viscosity that indicates that agglomerates are being sheared more than in a single pass mode. To reach an equivalent viscosity, again referring to Figure 4.3, a total of ten passes would be required or 30 minutes recirculation time.

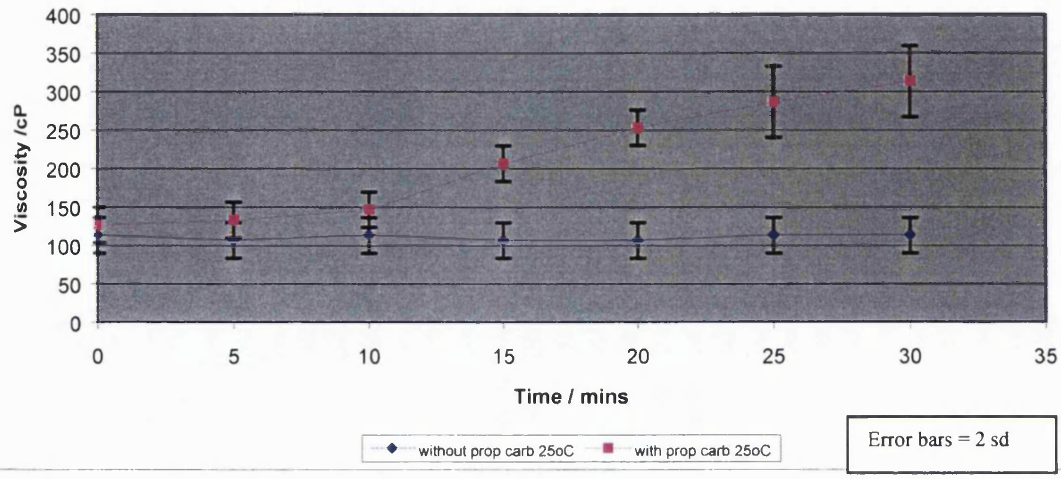
The advantage of using shear passes over continuous processing is for qualitative purposes only. It is possible to calculate the total shear rate applied and be confident that all clay agglomerates have experienced that shear rate. For each pass through the Silverson homogeniser, the particles experienced a shear rate 60,000 s^{-1}, and after ten passes, a total cumulative shear rate of 600,000 s^{-1}.

Once again, however, visual inspection of all the formulations led to the conclusions that at best, viscous liquids were produced that were highly unstable and prone to syneresis. This led to the conclusion that medium shear Silverson homogenisers, despite providing a significant shear rate and even with cumulative shear rates following multi-passes did not exert enough force to overcome the intermolecular forces of attraction that bind platelets together. Without doubt, agglomerates were broken down to a particle size that enabled a partial network of clay agglomerates that resulted in a viscosity build of the liquid. It was clear, however, that a structured gel network had not been achieved using this method of process and this was because full delamination, even in the presence of polar activator had not occurred. It is therefore possible to assume that the medium shear rate in combination with a polar activator may build a weakly structured semi-solid liquid, however, the dispersion of agglomerates will be limited to break down to a certain dimension, after which, further shear would have no significant effect on delamination.

4.7.4 The Effect of Medium Shear Mixing at 30kg Scale

The effect of scaling up the process using a Silverson Homogeniser with a double screen emulsifier screen was investigated.

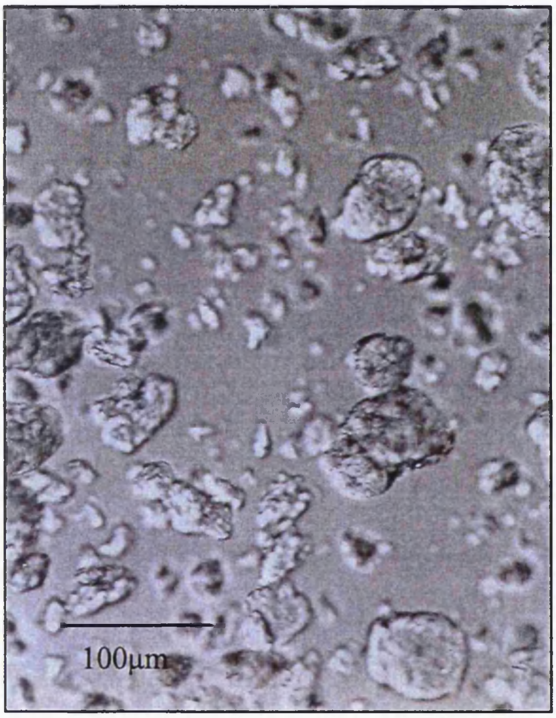
Figure 4.7 : Graph to show the effect of processing using double screen silverson on the mean viscosity of Bentone 38 formulations (Brookfield Viscometer TA@10rpm), n=3



The results of the graph in Figure 4.7 mirrors the results profile for that of the process on the laboratory scale Silverson mixers. Once again, viscosity remains fairly constant over time when a polar activator is not present but is seen to increase significantly when propylene carbonate is present. The overall viscosities after 30 minutes recirculation through the double screen Silverson are slightly lower than the viscosities obtained using the laboratory scale homogenisers and this can be attributed to the slightly lower shear rate that is exerted by the pilot plant scale homogeniser.

Optical microscopy images were captured at five-minute intervals during homogenisation of each formulation. A selection of the micrographs is shown in the following figures.

Figures 4.8 and 4.9 show micrographs of each formulation before homogenisation (denoted time = 0). Figure 4.8 represents the formulation of Bentone 38 and Silicone Fluid. Large agglomerates of Bentone 38 platelets are clearly evident that span a wide distribution of particle sizes up to approximately 60μm. Each agglomerate is a discrete entity and shows no sign of network formation. Figure 4.9 represents the formulation with polar activator. The physical appearance of the particles is noted to be slightly different from those in Figure 4.8 with a more textured appearance. This is believed to be a consequence of a difference in refractive index caused by the presence of propylene carbonate. The micrograph shows the presence of large agglomerates that again appear to be discrete entities. Particle sizes range up to 100µm. The increase in particle size may be due to intercalation of propylene carbonate causing Bentone 38 to swell. It may also be due to greater attractive forces existing between agglomerates in the presence of polar activator.



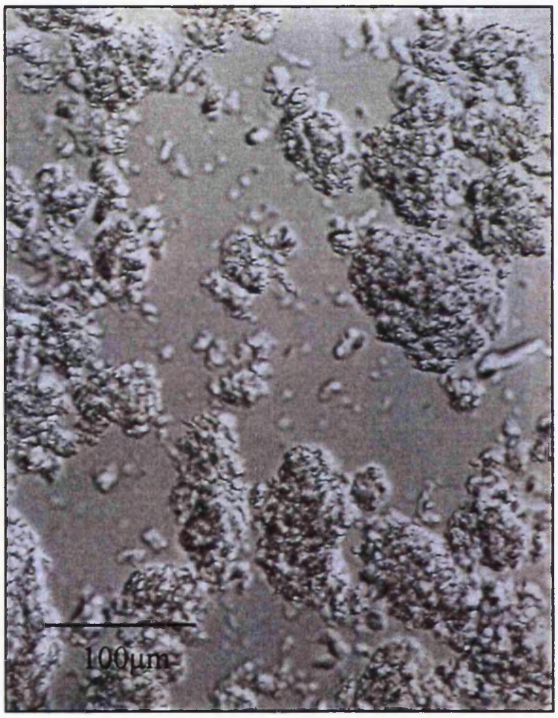
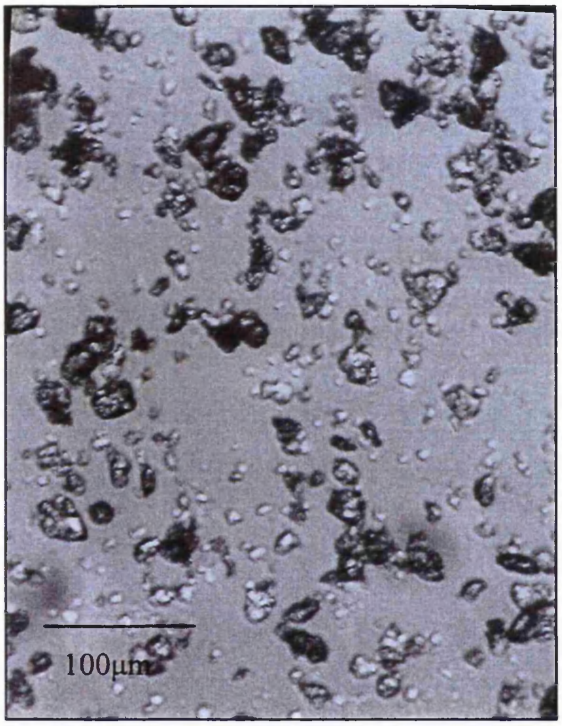


Figure 4.8 (left) : Micrograph of Bentone +Silicone sample T=0 (x20 DIC)
Figure 4.9 (right) : Micrograph of Bentone, Silicone + Prop Carb T=0 min (x20DIC)

Figures 4.10 and 4.11 represent the formulations after 15 minutes homogenisation through the double screen Silverson homogeniser. Both images display a decrease in particle size to approximately 40µm. The major difference between these two samples is that it would appear that the particles in Figure 4.10 appear to remain as discrete particles however reduced in size whereas the particles in Figure 4.11 seem to show signs of slight interaction. This would correlate the theory that a structured network develops in the presence of polar activator and when subjected to high shear. It should be noted that significant proportions of larger agglomerates are still present after fifteen minutes shear.



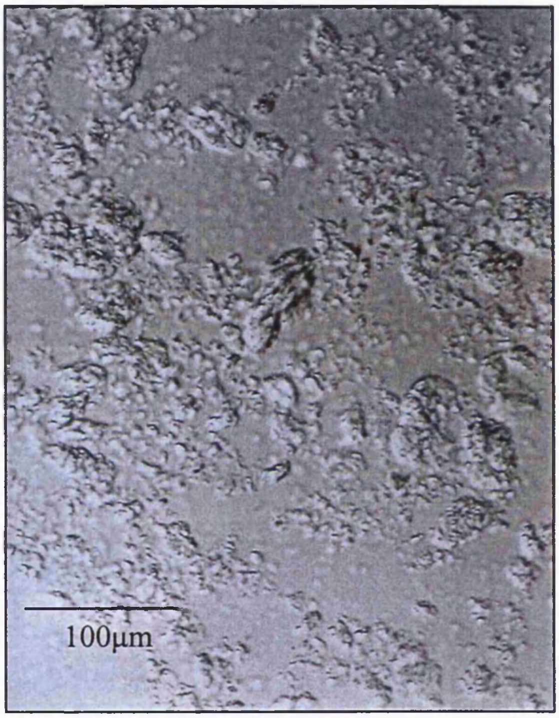
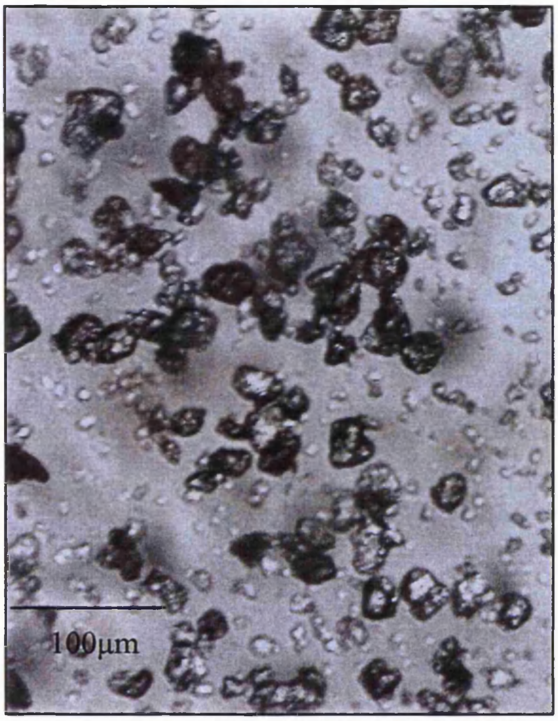


Figure. 4.10 (left): Bentone +Silicone sample T=15 min shear (x20DIC)
Figure 4.11 : (right) Bentone, Silicone + Prop Carb T=15 min shear (x20DIC)

Figures 4.12 and 4.13 represent images of each formulation after 30 minutes shear through the double screen Silverson homogeniser. The sample of Bentone 38 and Silicone fluid without polar activator (Figure 4.12) indicates that there is a distribution of discrete particles up to approximately 20 μm in diameter. Figure 4.13 shows the sample that contains propylene carbonate. It is clear that there are still a number of large agglomerates present (~ 60 μm in diameter) however there is a significant distribution of smaller particles of less than 10 μm. These smaller agglomerates appear to have formed a loose association that could be a macroscopic structure and is the network that has been described in the literature.



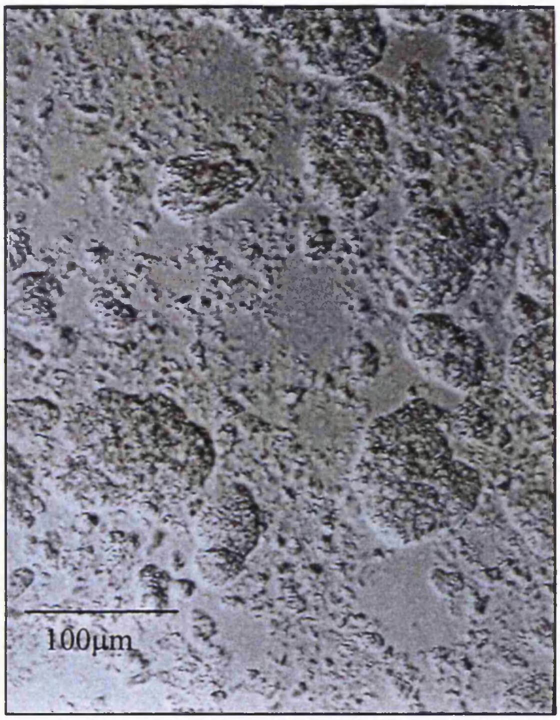


Figure 4.12 (left): Bentone +Silicone sample T=30 min shear (x20DIC)
Figure 4.13 (right) : Bentone, Silicone + Prop Carb sample T=30 min shear (x20DIC)

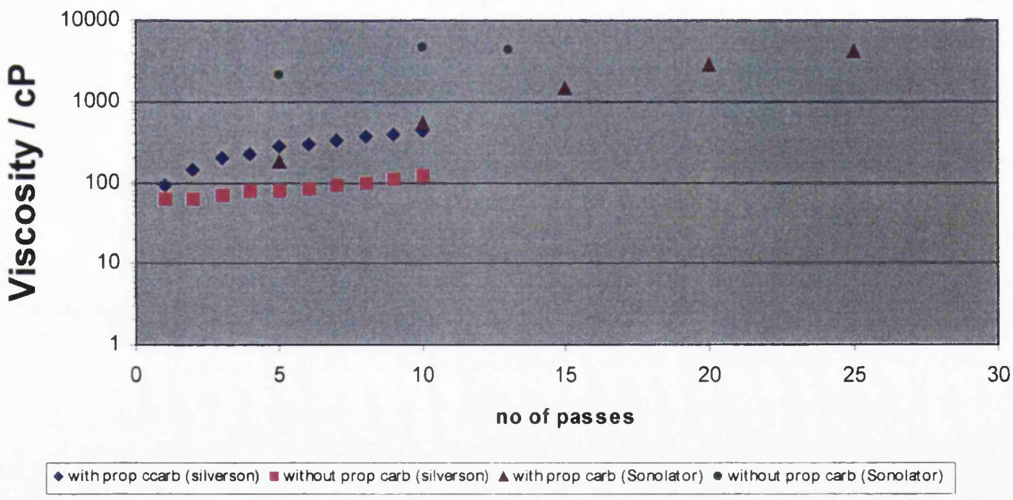
To summarise : The micrographs show that the formulation that does not contain propylene carbonate does not display any signs of particle interactions to form a network structure. It would seem that the shear applied by the double screen silverson homogeniser has an effect on partially reducing particle size of agglomerates to ~ 20 μm.

The micrographs of the formulation with polar activator show that there is a significant presence of smaller particles after shear through the homogeniser (30 minutes) that appear to form an attraction to each other. This evidence correlates to the significant increase in bulk viscosity observed with the sample that had been sheared for 30 minutes compared to the sample that had undergone no shear. This could be a result of an increase in inter-particle attractive forces or as a result of a greater number of particles present occupying a greater volume of space in the sample.

4.7.5 The Effect of High Shear Rate Mixing using a Sonolator

The sonolator was the next step up in the degree of shear applied to the formulations. A brief study using the Sonolator (Elida Fabergé, Leeds Pilot Plant) was carried out. Here, the results are shown in Figure 4.14. To display the differences in the effect of shear rate, the results of the medium shear studies on the laboratory scale Silverson L4R homogeniser are also displayed on the diagram.

Figure 4.14 : Graph to show the differences in viscosity (Brookfield Viscometer TA @10rpm) using different process equipment



The following comments can be drawn from the data:

- There is a significant increase in product viscosity for the formulations prepared using the Sonolator compared to the formulations processed using the Silverson Homogeniser. For example, after ten passes through the Silverson homogeniser, the viscosity of the product manufactured with propylene carbonate was equivalent to that manufactured on the Sonolator without polar activator.

- The product processed on the Sonolator (with propylene carbonate) has a viscosity with an order of magnitude greater that either the equivalent formulation made on the Silverson or the polar activator free system.

- The formulation without propylene carbonate that is manufactured using the Sonolator required as many as 25 passes to reach an equivalent bulk viscosity as that manufactured using the same methodology with a polar activator.

Optical microscopy images were taken of samples throughout the process. A selection of the micrographs are shown in the following figures.

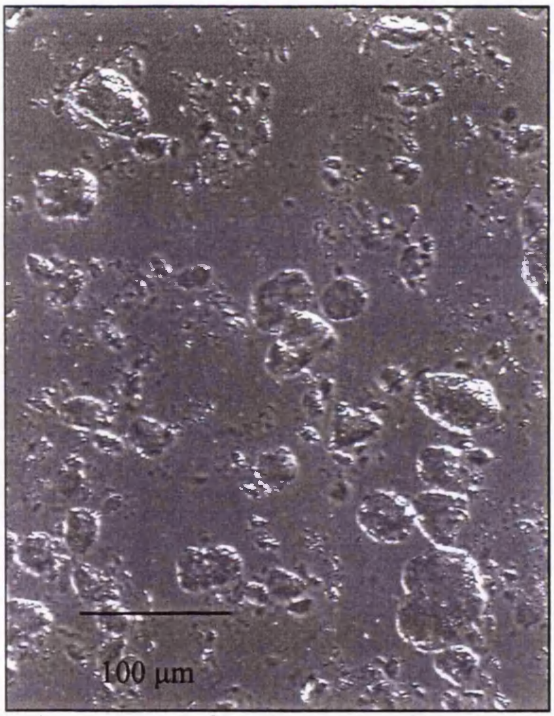


Figure 4.15 (left) : Bentone + silicone sample 5 pass through Sonolator (x20 DIC)
Figure 4.16 (right) : Bentone + Silicone + Prop Carb sample 5 pass through Sonolator (x20 DIC)

Figure 4.15 represents a micrograph of the formulation without propylene carbonate that has been subjected to five passes through the Sonolator. The image displays a broad range of agglomerate sizes ranging from below 10µm to approximately 60 µm.

Figure 4.16 represents the micrograph of the formulation that contains polar activator (propylene carbonate). This has also been subjected to five passes through the Sonolator. It is clear from this image that there is a significant difference in particle size when propylene carbonate is present. The micrograph shows that almost all the agglomerates have been dispersed to particles of less than 10 μm in diameter. A small proportion of agglomerates of larger dimensions still are apparent, however these are minimal in number.

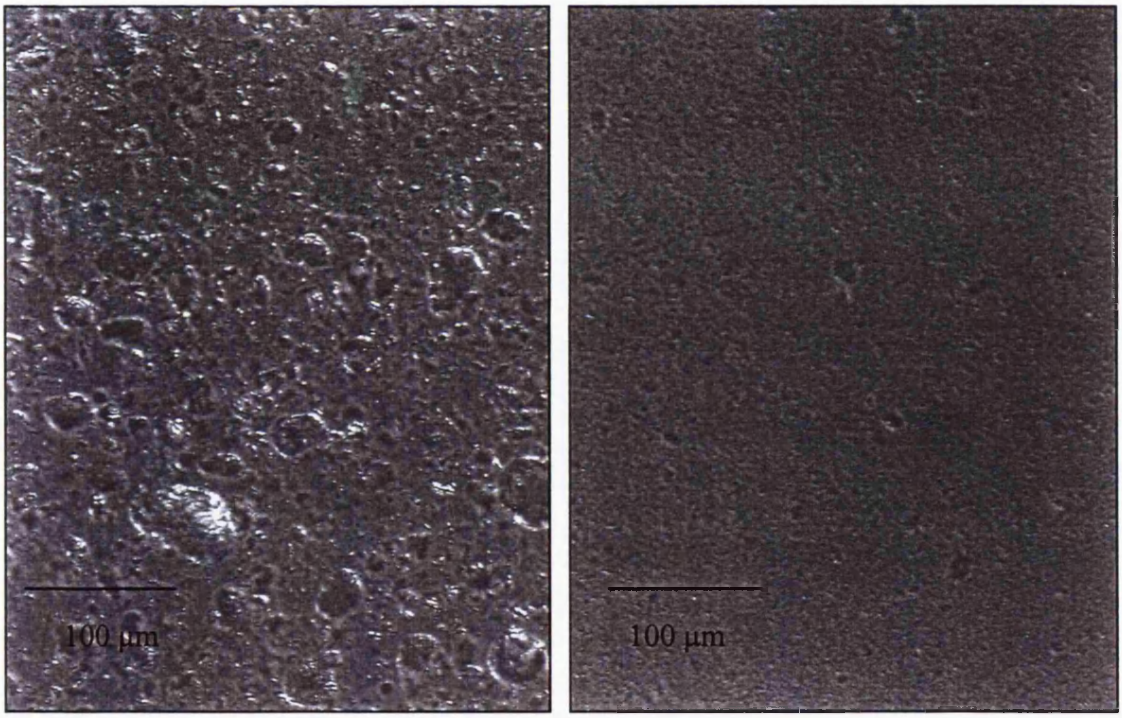


Figure 4.17 (left): Bentone + Silicone sample 10 pass through Sonolator (x20 DIC)
Figure 4.18 (right): Bentone + Silicone + Prop Carb 10 pass through Sonolator (x20 DIC)

Figures 4.17 and 4.18 represent the same formulation after ten shear passes through the Sonolator. The sample of Bentone 38 and Silicone fluid (Figure 4.17) displays a greater proportion of small agglomerates (<10 μm) than was observed on the micrograph of the sample that had five shear passes however there is still a significant proportion of fairly large agglomerates (40-60μm). The micrograph of the sample that contains polar activator is significantly different exhibiting nearly complete deagglomeration to particles with dimensions less than 10 μm.

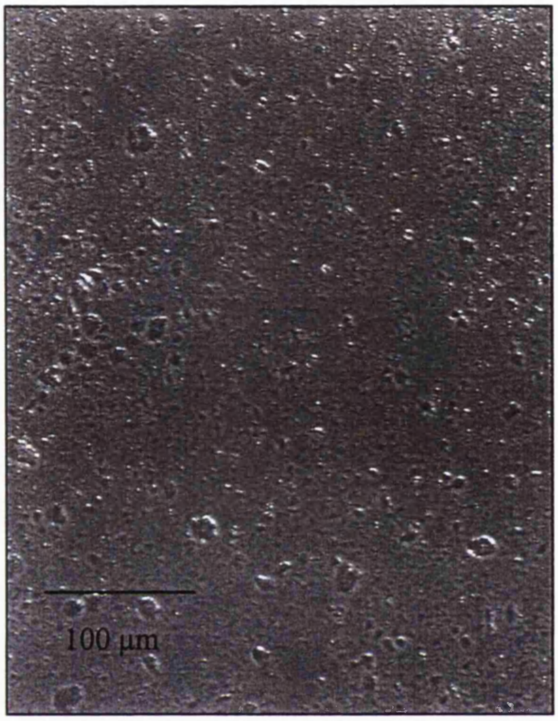


Figure 4.19 : Bentone + Silicone sample 25 pass through Sonolator (x20 DIC)

Figure 4.19 represents the sample of Bentone 38 and Silicone fluid that had experienced 25 shear passes through the Sonolator. It is clearly evident that even after 25 shear passes there are still a number of particles in the region of 20 μm. The majority of particles present however are significantly smaller than 10 μm.

To summarise : Referring to the micrographs representing the Bentone and Silicone fluid formulation, it is evident that after 5 passes through the sonolator, the greater proportion of particles are fairly large agglomerates (size range ~ 40 - 50μm diameter). With increasing shear passes, it is evident that these agglomerates are beginning to be broken down into smaller agglomerates (dimensions ~ 10μm) and there is an increasing number of smaller particles present. However, despite increasing the number of shear passes through the sonolator, it is not until 25 passes have been made that the majority of agglomerates have been dispersed to particles of dimensions <10 μm effectively and a gel is formed.

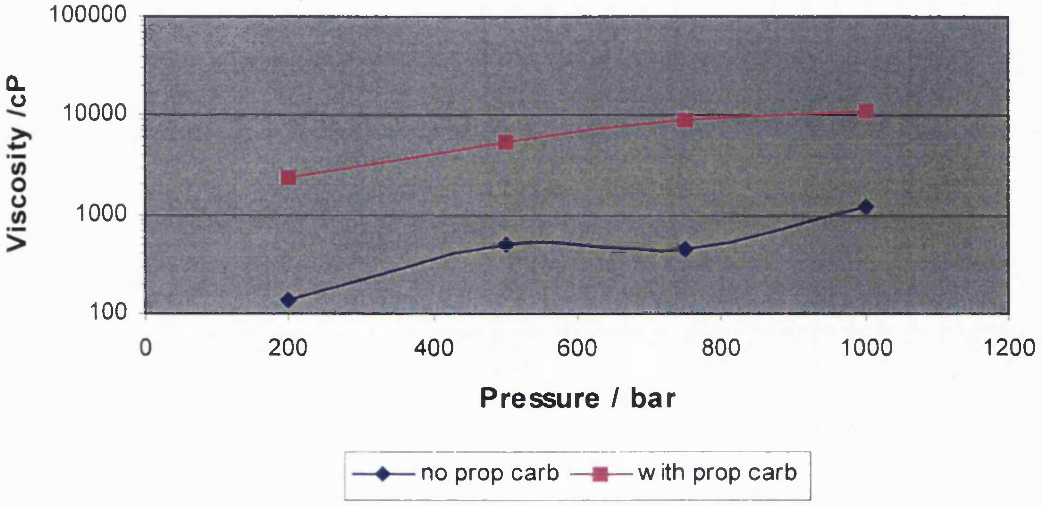
The gel formed after 25 passes was quite stable showing only very small amounts of visible syneresis of silicone fluid. The samples taken throughout the experiments were noted to be unstable and showing visible signs of sedimentation of solid materials. This would correspond to large agglomerates sedimenting under gravitational forces.

The micrographs of the samples with propylene carbonate show a significantly different picture to that displayed for the micrographs where propylene carbonate is absent. After only 5 passes through the sonolator, nearly all of the large agglomerates of Bentone 38 have been effectively dispersed. The major proportion of platelets appears to be dispersed evenly throughout the slide. By ten passes, only a few small agglomerates remain and the particles are fully dispersed and the majority of particles are of a uniform size. Again, these correlates to the visual inspection, where the samples from ten and thirteen sonolator passes had a gel-like consistency that appeared stable and did not display evidence of syneresis.

4.7.6 The Effect of Very High Shear Rate Processing

Figure 4.20 shows the initial results of experiments that were performed using the very high shear rate of the Rannie Minilab homogeniser. This graph shows the results of a single pass of each formulation through the homogeniser set at different operating pressures. (Please note that the results on this and the following graph are for single sets of data). The viscosities were measured using the TA spindle at 10 rpm and data are plotted on a logarithmic scale. These data do show a clear trend that will allow a certain degree of confidence in the results.

Figure 4.20 : Graph to show the effect of single pass homogenisation through Rannie Minilab at different pressures vs bulk viscosity



From these data it is possible to say :

- Increasing the process pressure from 200 to 1000 bar increases the product viscosity for formulations manufactured both with and without polar activator. As with all the previous experiments, for overall viscosity, this has the most significant effect on the formulation with the polar activator being an order of magnitude greater than the formulation manufactured without an activator.
- Viscosity of the organoclay bases increases significantly at the upper region of the pressure range tested with a marked increase of product viscosity for that processed at and above 750 bar.

There are two points to note regarding this series of experiments.

1. It was not possible to maintain a constant temperature during the processing of the organoclay bases using the high pressure homogeniser since the homogenising valve is housed in a solid stainless steel block that retains heat as increasing pressure is applied. Therefore a temperature differential is always noted and is usually in the temperature range of 20-30°C. It is not possible therefore to assume that the gel

formed is a result of mechanical processing alone since the thermal energy generated during the process may contribute to delamination of platelets.

2. The shear rate increases as process pressure is increased. To achieve the desired process pressure, a hand-operated handle is turned to reduce the gap between the valve and its impact ring. Since flow rate of the fluid is maintained at effectively a constant rate, by means of a piston pump, pressure is built by forcing the same amount of fluid in the chamber through a smaller gap. Therefore as pressure increases, so too does the shear rate. Viscosity measurements were therefore dependent upon shear rate exerted at certain pressures.

4.7.7 The Effect of Double Pass Process through Minilab Homogeniser

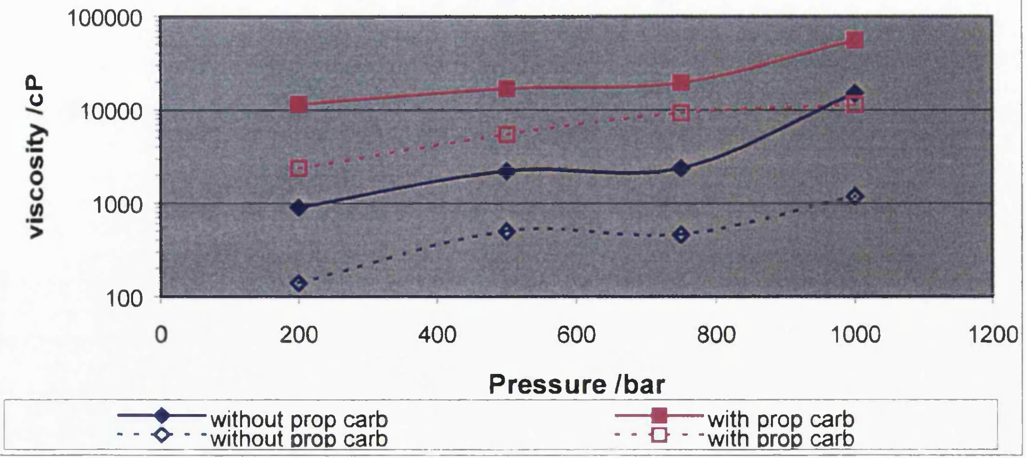


Figure 4.21 :Graph to show the effect on bulk viscosity by double pass processing through Minilab Homogeniser at different pressures (N.B. 1st pass = 1000 bar. Dotted lines represent single pass only)

The effect of a two-pass homogenisation process has a profound effect on the viscosity of the formulations with an increase in an order of magnitude for each formulation. The two-pass process comprises of the entire product being passed through the homogeniser followed by a second complete pass. The viscosity data are displayed on a logarithmic scale and the results of a single pass are depicted by the dotted line to serve as a comparison. (Figure 4.21) Once again it was only possible to record single data records, however it is possible to determine a definite trend in the results obtained.

A number of trends may be drawn from this data:

- A single high pressure pass at 1000 bar compared with a dual pass of a high pressure pass (1000 bar) followed by a low pressure pass (200 bar) did not alter the end viscosities for either formulation.

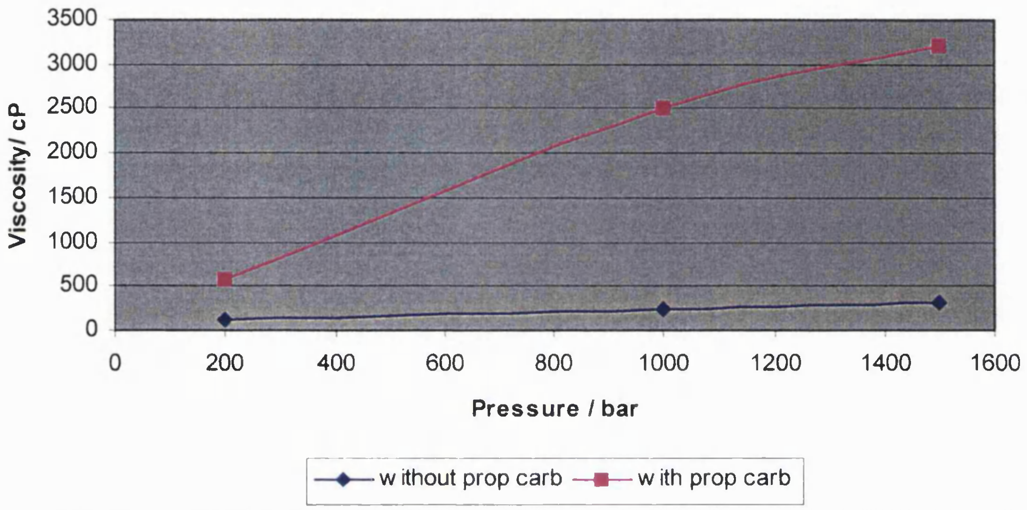
- Comparison between a single pass and a dual pass through the homogeniser was that a significant increase in viscosity was noted for both formulations indicating that delamination was not optimised by a single pass through the homogeniser. An alternative reason for this was that effective delamination did occur with a single pass at 1000 bar but a second pass re-aligned the platelets to provide a more ordered structure.

- Two high pressure passes (2 x 1000 bar) gave the greatest bulk viscosity measurements and were the most significant in step change of final viscosity.

4.7.8 The Effect of Very High Shear Homogenisation on APV Lab 2000

Figure 4.22 shows the viscosity data for the formulations with and without polar activator that had undergone one shear pass through the Lab 2000 homogeniser. Viscosities were measured using the TB spindle (c.f. TA spindle as previously) at 10 rpm. The Lab 2000 model has an upper limit of 2000 bar pressure however samples were only run up to 1500 bar. Temperature was maintained as constant as possible by placing a cooling coil around all the pipework both before and after the homogenising valve to maintain temperature at approximately 13°C. Once again it was not possible to control the temperature differential at the homogenising valve however, it is assumed that with the cooling coil in position, the temperature rise did not cause a phase transition and have an effect on process.

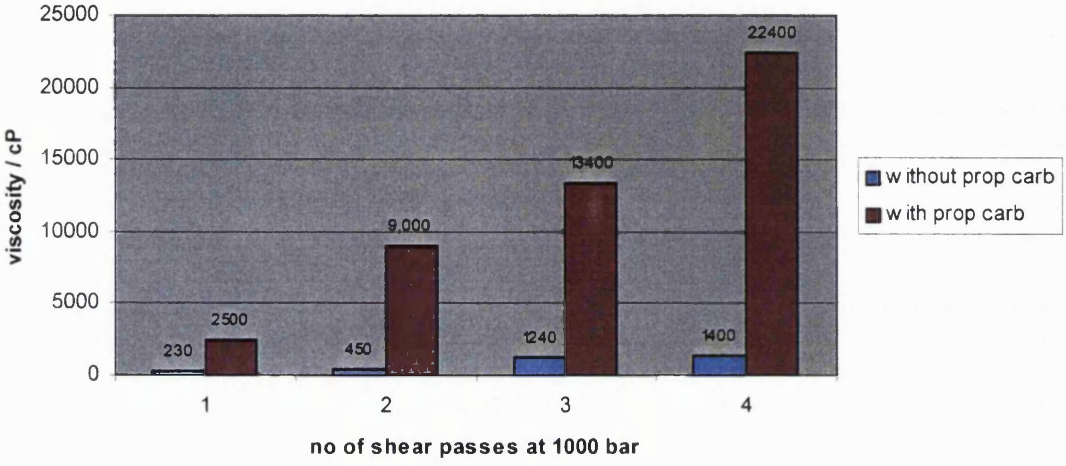
Figure 4.22 : Graph to show the effect of a single shear pass through APV Rannie 2000 homogeniser at different process pressures on bulk viscosity



The results shown are the mean values for experiments that were run in triplicate. Again, the same trend in viscosity rise is noted for the samples that had polar activator. A single pass at 1000 bar produced a viscosity five times that processed at the lower pressure of 200 bar. Viscosity increases almost linearly as process pressure and therefore shear rate is increased. This indicates that the more work performed on the system, the greater the delamination. The samples without polar activator do not increase in viscosity to the same degree as when polar activator is present.

Figure 4.23 shows the mean values for viscosity after shear passes through the homogeniser. The results show that when polar activator is not present, even after four passes, the viscosity is just over half that as to when the formulation with propylene carbonate undergoes one pass through the homogeniser. This highlights the significant contribution role that propylene carbonate plays in creating a highly viscous gel.

Figure 4.23 : Graph to show the mean viscosities of product viscosity after shear passes through Rannie 2000 homogeniser at 1000 bar



Again, the sample with propylene carbonate displays a linear increase showing that viscosity is directly proportional to the number of shear passes. The contribution that propylene carbonate gives to structuring implies that there must be weakening of the intermolecular forces that bind the agglomerates together thus less mechanical shear is required to deagglomerate the particles. In addition, a truly stable gel can be manufactured and refined with increasing shear passes.

Visual inspection of the samples are shown in Figures 4.24 and 4.25. These images were taken with a digital camera and show what is meant when reference is made to a suspension and a gel. In Figure 4.24, it is quite clear that the right hand sample is a thick, stable, homogeneous mixture with a texture similar to a gel. It has a smooth consistency with a glossy appearance. The other sample in the image displays an unstable sample that has undergone sedimentation. This sedimentation takes place in a matter of minutes.

The image in Figure 4.25 shows the differences between the two formulations. The samples with propylene carbonate are clearly gelled samples as they retained shape after being poured into the vessels. The samples without propylene carbonate show the

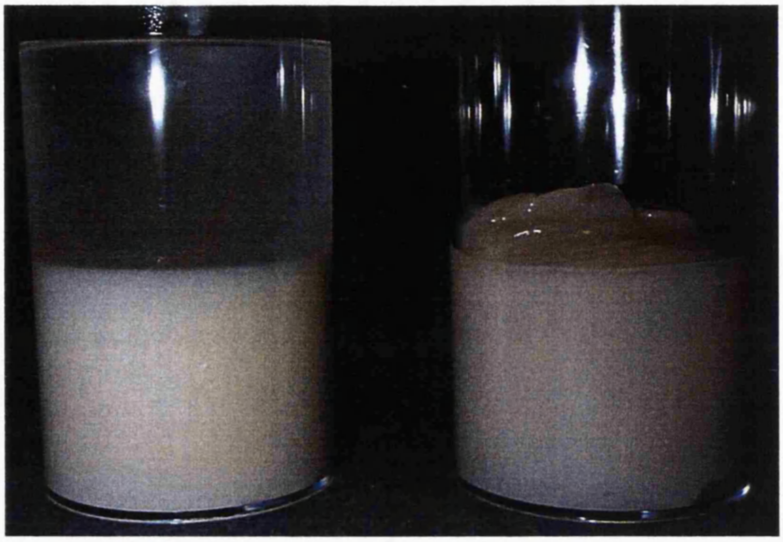


Figure 4.24 Digital image of sedimentation and a Bentone 38 gel processed on APV Rannie

Left hand sample : Bentone 38 + Silicone Fluid 200 bar 1 pass (sediementation)
Right hand sample : Bentone 38, Silicone Fluid + Prop Carb 1000 bar 2 passes (gel)

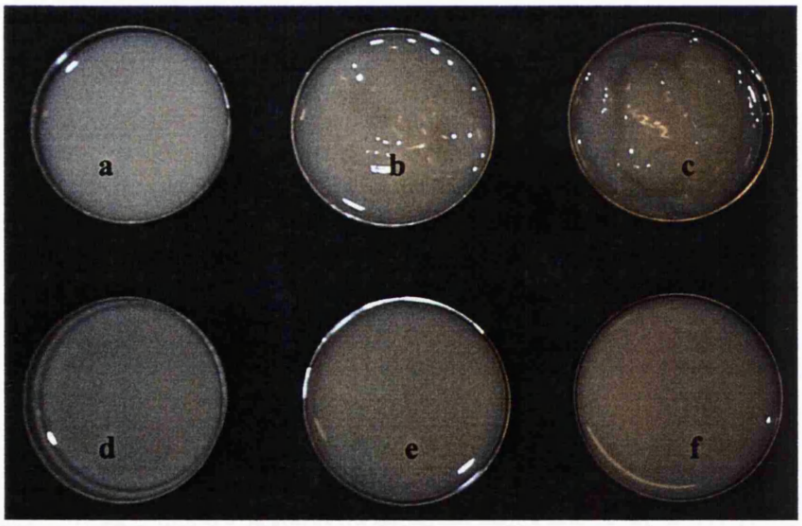


Figure 4.25 :Digital images of Bentone 38 suspensions and gels processed on the APV Rannie

a)	With polar activator	200 bar (1 pass) – thickened liquid
b)	With polar activator	1000 bar (1 pass) – gel
c)	With polar activator	1000 bar (2 pass) - gel
d)	Without polar activator	200 bar (1 pass) – sedimented solids
e)	Without polar activator	1000 bar (1 pass) – thickened liquid, some syneresis
f)	Without polar activator	1000 bar (2 pass) – viscous liquid, slight syneresis

transition from a highly unstable form to a stabilised liquid/gel consistency. The sample that has undergone two shear passes through the homogeniser, although at a much lower viscosity compared to that of the one manufactured with propylene carbonate was noted to be very stable.

The samples were imaged using optical microscopy. The micrographs are representative of images taken for each of the samples.

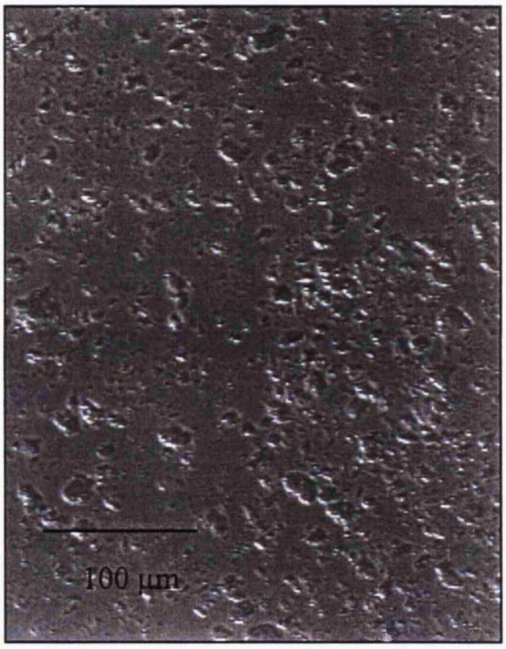


Figure 4.26 (left) : Bentone and Silicone Fluid sample, 1x200 bar pass through Rannie Homogeniser (x 20 DIC)
Figure 4.27 : Bentone and Silicone fluid sample, 1x1500 bar pass through Rannie Homogeniser (x 20 DIC)

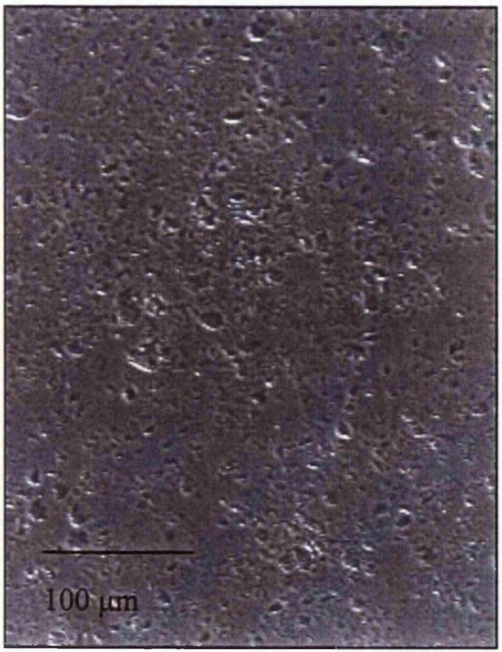
The following observations can be made:

- Note the large agglomerates present in Figure 4.26 that represents a sample of Bentone 38 and Silicone fluid that has had one shear pass through the homogeniser at 200 bar. There are very few primary particles present in this image indicating that delamination of particles is not efficient.
- Increasing the pressure from 200 bar up to 1500 bar Figure 4.27 increases the shear rate sufficiently to disperse the agglomerates. It should be noted that there are still

agglomerates present, however they are significantly reduced in size. This implies that the shear exerted on the agglomerates simply ruptures the larger agglomerates to yield smaller dimension agglomerates rather than peeling off layers of clay.

- Figures 4.28 and 4.29 shows the same pressure process passes (1 x 200 bar and 1 x 1500 bar), this time with propylene carbonate present. The images are significantly different from the images of the samples without polar activator. At 200 bar pressure, there is a wide range of polydisperse agglomerates, however their dimensions are significantly less than those in Figure 4.27. As the processing pressure is increased, the agglomerates are observed to have dispersed into far more uniform particle size. This correlates to the significant viscosity rise seen in Figure 4.23 and the transformation from a liquid to a gel. This indicates that the more dispersed the particles are, the greater the number of interparticle forces of attraction there are between agglomerates and thus the observation of a more stable and robust gel network.
- Increasing the number of shear passes at 1000 bar from 1 to 4 passes, further refines the particles down to what is most likely their primary state. Figure 4.30 represents the sample without polar activator that has had four shear passes through the homogeniser. Note that full dispersion has not occurred even after four passes at 1000 bar pressure although after four passes, a greater number of primary particles seem to be observed. Conversely, the equivalent sample formulated with polar activator (Figure 4.31) seems to undergo a significant reduction in particle size which would indicate that propylene carbonate becomes more and more intrinsically mixed with the clay and enables the platelets to swell and disperse more effectively.

Figure 4.28 (left) : Bentone, Silicone + Prop Carb, 1 x 200 bar pass (x 20 DIC)
Figure 4.29 (right): Bentone, Silicone + Prop Carb, 1 x 1500 bar pass (x 20 DIC)



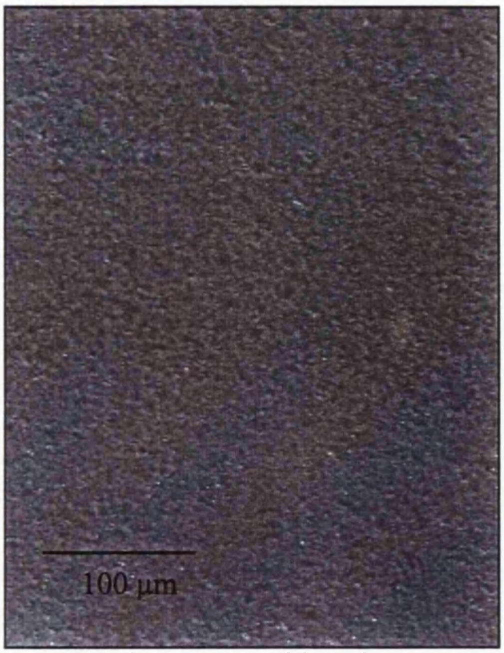


Figure 4.30 (left) : Bentone + Silicone sample, 4 x 1000 bar pass (x 20 DIC)
Figure 4.31 (right) : Bentone + Silicone + Prop Carb sample, 4 x 1000 bar pass (x 20 DIC)

4.7.9 Rheological Profile of Bentone 38 Gels

4.7.9.1 Yield Stress Measurement

Figure 4.32 : Graph to show the effect of viscosity and yield stress as shear stress is increased of Bentone 38 gels using Carri-med rheometer

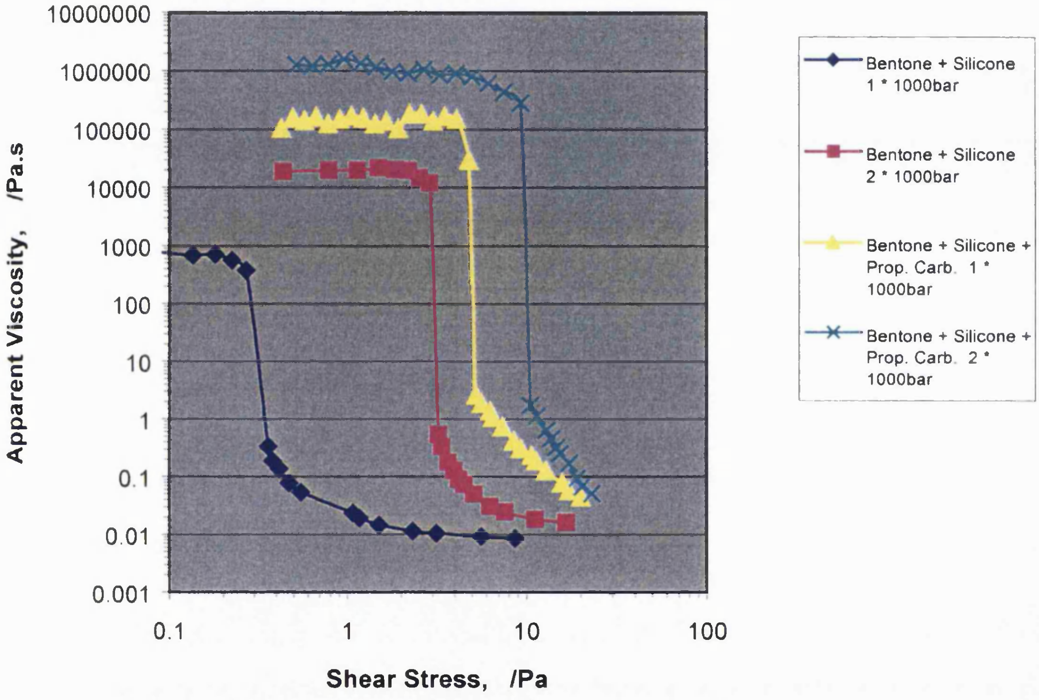


Figure 4.32 represents the rheological profile measuring the yield stress of the gels manufactured with and without propylene carbonate after single and dual passes on the Lab 2000 homogeniser. The y axis represents viscosity in Pa.s and the x axis represents the applied shear stress measured in Pa. The rheological profile provides information on the product stability and the structure. An increase in viscosity indicates a more ordered microstructure.

As has been reflected in Brookfield viscosity measurements previously, the most viscous product was the sample that had polar activator and had undergone two shear passes through the Lab 2000 homogeniser. Next in sequence is the sample with polar activator and has undergone one shear pass. In the same order, but with reduced viscosities are the two samples without propylene carbonate. The viscosities measured on the carri-med rheometer also reflect the significant difference in viscosity of the polar activator free sample after a second homogeniser pass as observed in the earlier experiments.

The data on the graph show that at a certain shear stress there is a rapid drop in viscosity over several orders of magnitude for each of the samples. This is indicative of the shear stress required to literally 'break' the structure and is termed the apparent yield stress of a product. This is the amount of shear stress that is required to overcome the intermolecular forces that exist in the microstructure of the sample. Therefore, this is the data that provides the information on the stability of the network i.e. the greater the shear stress the more stable the microstructure.

The data shows that the sample with the greatest stability and therefore the highest degree of structuring is the dual pass organoclay with polar activator and the weakest network was that of the single pass, no polar activator sample. Again, this data correlates with previous observations and the conclusion that the sample that has the greatest degree of dispersion yields the strongest gel both in stability and viscosity. With increased dispersion of primary particles, there are a greater number of intermolecular attractive forces that require a greater amount of shear stress to break the links that hold the microstructure.

4.7.9.2 Comments

The technique for measuring the apparent yield stress of the clay suspensions uses a vane and basket geometry. This geometry is a measuring system that introduces minimal disturbance into a sample when performing steady shear flow experiments.

This is particularly important on shear sensitive systems such as clay suspensions. Viscoelastic measurements were considered however there are a number of reasons why yield stress was selected over viscoelastic properties. The main reason was the practical issues of sample testing Bentone 38 gels.

The vane and basket has not been proven for oscillatory measurements whereas the cone and plate that is conventionally used for measurement of viscoelastic properties is well understood (Barnes, 1997). Barnes details the issues that arise in sample preparation for viscoelastic measurement and the distortions to the results that can arise. For example, The structure of sample is massively disturbed when the plates are brought together to measure the gap setting (~1 mm). This squeezes the product to form a film-layer by subjecting the product to a reasonable amount of extensional distortion.

There is also no control of the rate of ramming the cone up and down during the experiments that also causes product deformation prior to measurement. The cone and plate also has a greater surface area to volume ratio compared to the vane and basket causing volatile materials (silicone fluid and alcohols) to evaporate off during the experiment even in the presence of a solvent trap.

Finally, since the formulations are composed essentially of silicone fluid and inherently weak systems prone to sedimentation, the samples tend to 'slip' and experience wall effects even when a roughened cone and plate is used. The vane and basket geometry uses a greater volume of sample and minimises these effects.

Consequently viscoelastic measurements are not readily compatible to samples of Bentone 38 and volatile silicone fluid gels that are not intrinsically stable and can be prone to rapid sedimentation. Therefore yield stress measurements were concluded to provide more information on product structure and stability.

4.7.10 DSC Profile of Bentone 38 Clay

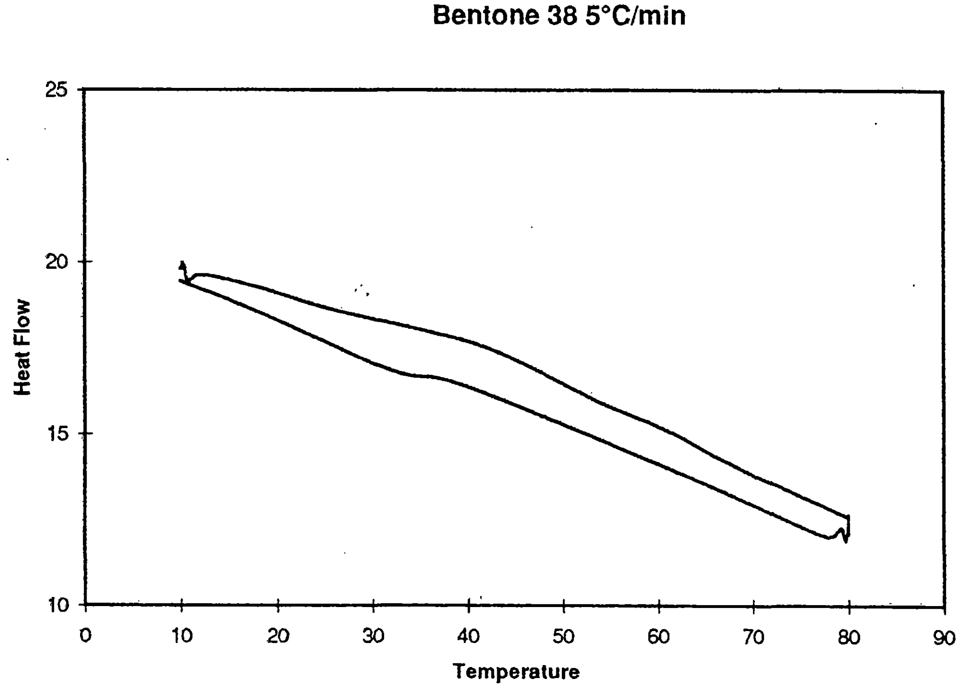
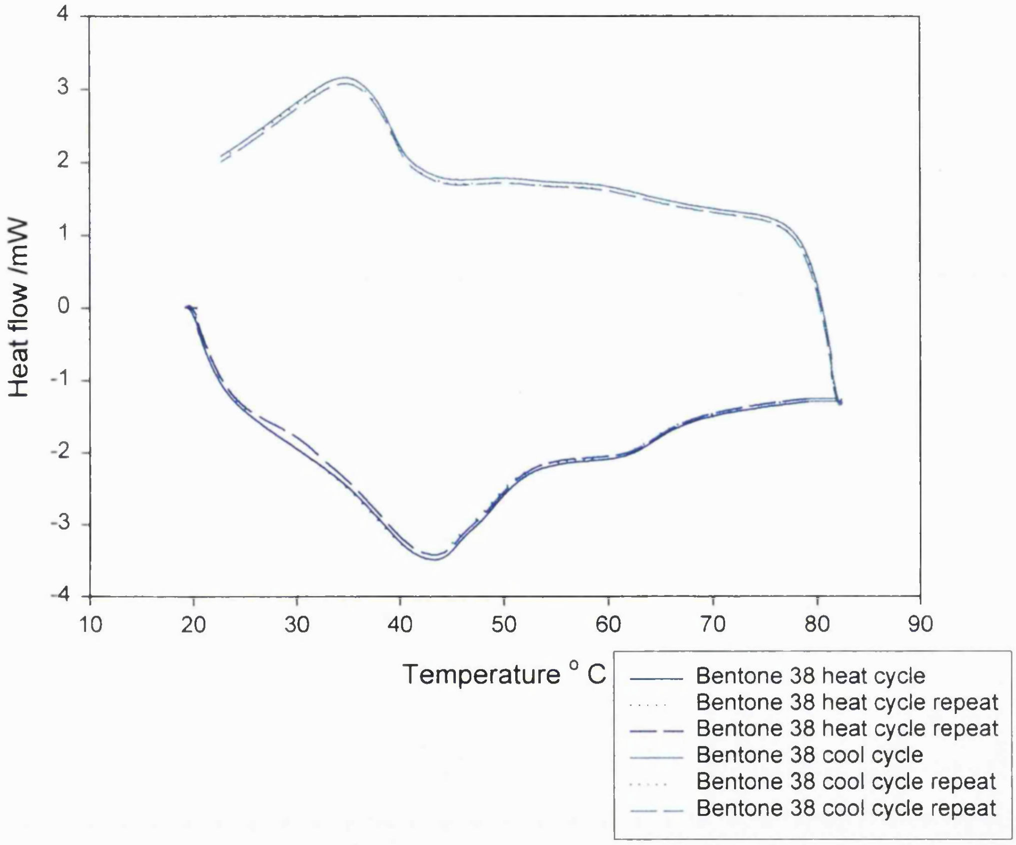


Figure 4.33 : DSC plot for Bentone 38 clay

Figure 4.33 shows the plot for Bentone 38 sample run using Conventional Differential Scanning Calorimetry. The results show no apparent phase change for Bentone 38. Note the heat and cool cycles were very rapid (5°C/min) and therefore any slight phase change may not have been observed. However, it was decided that a more sensitive instrument would be required to pick up any subtle phase transitions considering the ratio of clay to organic material in a Bentone 38 sample.

The following figures represent a series of experiments performed at the London school of Pharmacy using the Micro III Setaram High Sensitivity Differential Scanning Calorimeter. The first graph in the series is that of Bentone 38 and is shown in Figure 4.34. To qualify reproducibility, results for each run was plotted.

Figure 4.34 : Graph to show heat flow of Bentone
over temperature range using HSDSC
Sequence = 20 - 80°C, rate = 1°K/min



It should be noted that there was no stable baseline for any of the plots. This is attributed to the fact that Bentone 38 is a commercial material and is not graded. It is therefore likely that the quaternary on the surface of the clay is not pure and carries a significant quantity of impurities. Also it should be noted that there are also two methyl groups that would melt at a much lower temperature than the alkyl carbon chains. As such, focus on the trend of the maximum peaks should be considered only.

The following observations can be made.

- Each run was run independently using a fresh sample each time and it can be noted that the results for Bentone 38 were highly reproducible.

- There is a maximum peak on the heating curve at approximately 43°C and the curve spans across a temperature range of between 30 – 60°C. This indicates clearly that a phase change is occurring and it is assumed to be the alkyl groups of the quaternary ammonium compound on the surface of the clay.

- A shoulder is observed at approximately 55°C on the heating curve. This is probably a small quantity of higher alkyl chain organic since the quaternary ammonium compound is sourced from tallow (mainly C18) and therefore could be a contaminant.

- The cooling curve mirrors the shape of the heating curve indicating that recrystallisation is occurring. This begins at approximately 40°C that correspond to the recrystallisation of C18 alkyl chains.

Figure 4.35 shows the data of further HSDSC studies of Bentone 38 dry, Bentone38 and Silicone Fluid and Bentone 38, Silicone Fluid and Propylene Carbonate.

It should be noted that the temperatures of the samples with silicone present were not taken above 60°C. This is because this would have taken the silicone to within its flashpoint range and, since the calorimeter was not deemed intrinsically safe or zoned for flammable materials, it was impractical to take these samples to higher temperatures.

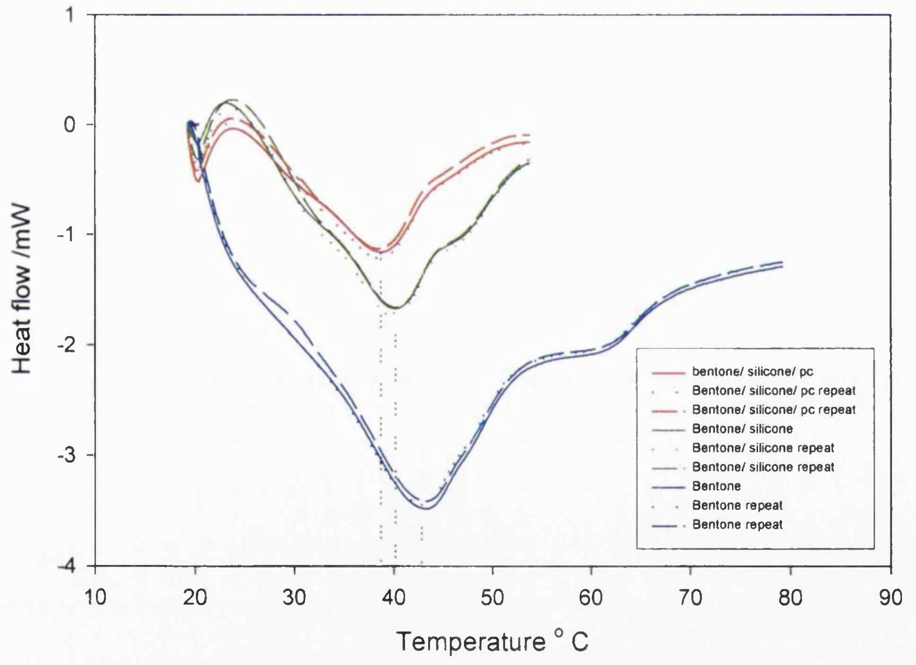
The following observations may be made:

- The amount of heat flow was greatest for the dry Bentone 38 sample. This is due to the dilution factor that occurred with the addition of the liquids in the other two formulations.

- The shape of each of the curves was identical, each one displaying a shoulder that, as mentioned before, was likely to be contaminants in the organic phase.

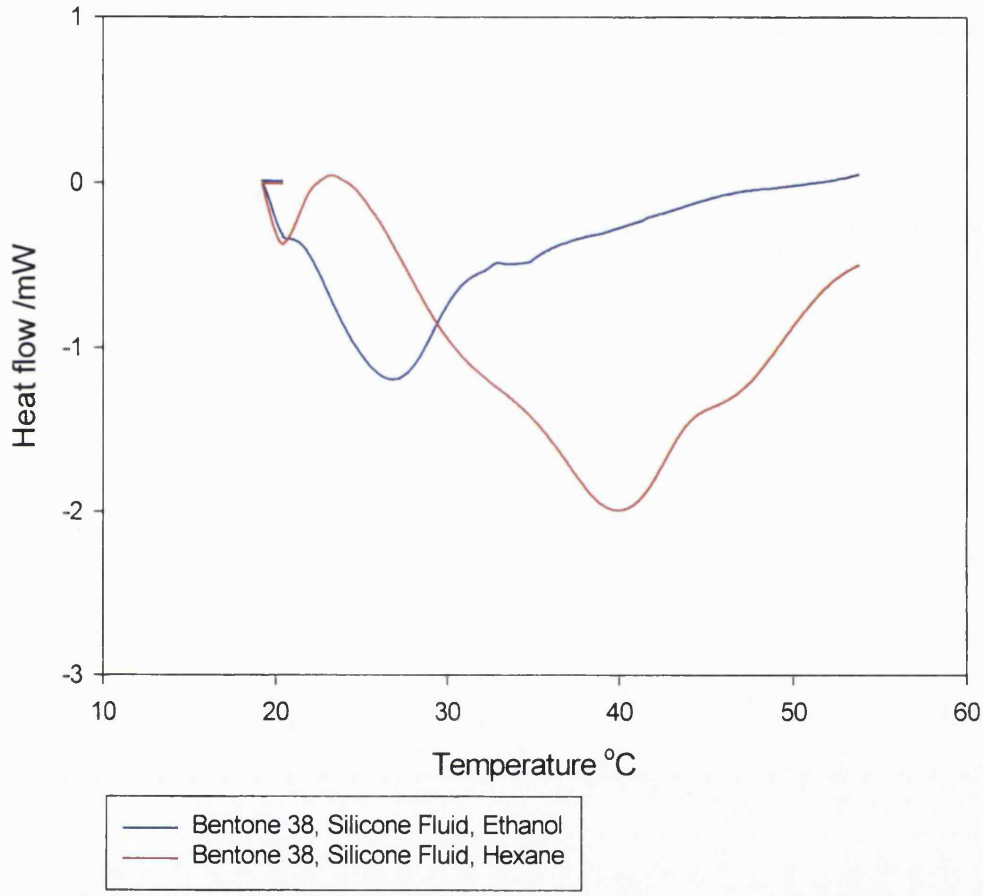
- There was a clear phase transition for each of the samples, however, with the addition of silicone and propylene carbonate the maximum peak was observed to be slightly lower in temperature respectively. This temperature decrease in maxima was assumed not to be significant. Interestingly the lowest temperature peak was that of the propylene carbonate and this could be attributed to some slight solubility of the quaternary ammonium in the presence of the polar activator.

Figure 4.35 : Graph to show heat flow of Bentone and Bentone/Silicone suspensions with and without propylene carbonate (pc) over temperature range using HSDSC. Sequence = 20 - 80°C, rate = 1° C/min



Further studies were also performed on the HSDSC investigating the effect of ethanol (polar activator) and hexane (non-polar). The results are represented in Figure 4.36

Figure 4.36 : HSDSC plot
Bentone and Silicone Fluid with Ethanol/Hexane
Heat cycle 20 - 60°C, rate = 1° C/min



The plots show a couple of points to note:

- The heat curve for the sample manufactured with hexane was identical to that of the one with silicone fluid. This would indicate that hexane was inert in the system, having no chemical effect on the quaternary ammonium compound.
- The sample manufactured with ethanol gave significantly different results to the previously tested samples. There is a clear phase transition in the region of 20 to 30°C, that is 10 degrees lower than the samples with silicone and activators and dry Bentone 38. The most likely explanation for this phenomenon is that the quaternary

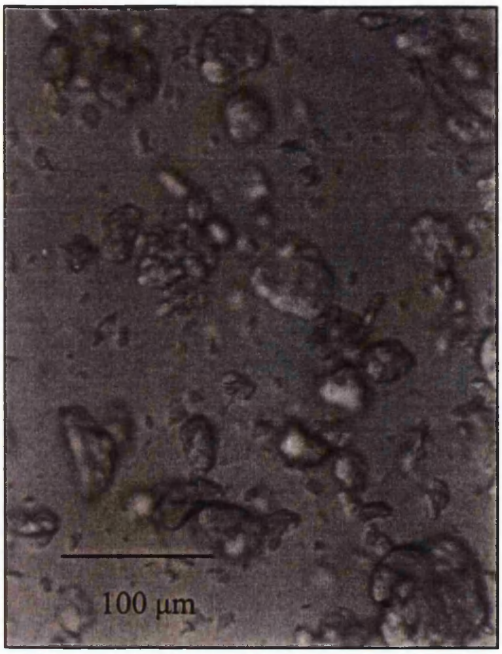
ammonium partially solubilises in the presence of ethanol, which is enhanced as the mixture is heated and therefore a phase transition from semi-solid to liquid occurs at a lower temperature.

From these results, it can be concluded that a definite phase transition occurs with heating Bentone 38 to at least 50°C in the presence of propylene carbonate, silicone or hexane. From the results of the ethanol study, it is possible to propose that different polar activators may alter the temperature range at which this phase transition may occur. For the systems that this work is focusing on heating the clay systems to 50°C is a practical working temperature for processing in a laboratory using conventional heating systems without volatilising the silicone fluid from the system or over-shooting its flashpoint.

4.7.11 Effect of Temperature on Structuring using Low, Medium and Very High Shear Rates

Table 4.1 displays the viscosity measurements of the processing studies performed at elevated temperature (50°C). Figures 4.37 to 4.40 also show micrographs of the optical microscopy images for each of the samples taken after the process.

The microscopy images clearly show that at low shear and medium shear there are a large proportion of polydisperse agglomerates present that is reflected by the product viscosity being so low. Particles range from a few microns to over 50μm in diameter. However, the image of the very high shear passes through the high pressure Rannie homogeniser indicates that particles have under gone significant particle size reduction. The distribution of agglomerates is significantly more uniform with only a few agglomerates of diameter measuring approximately 10 microns



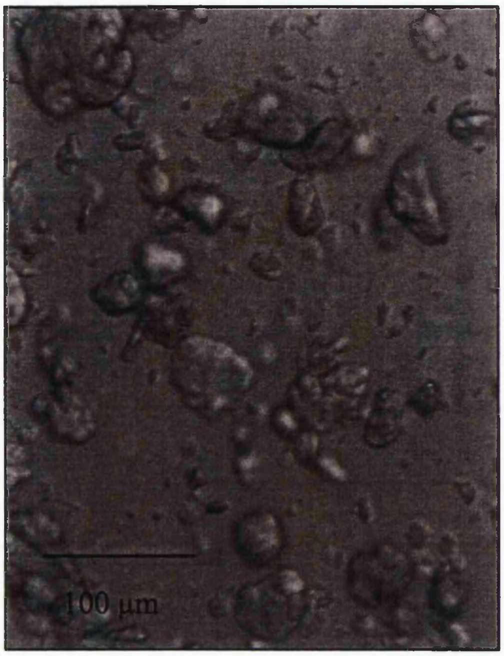


Figure 4.37 (left) : Bentone 38 + Silicone fluid sample processed using Heidolph @ 50°C (x 20 DIC)

Figure 4.38 (right) : Bentone 38 + Silicone Fluid sample processed using Lab. scale Homogeniser @ 50°C (x 20 DIC)

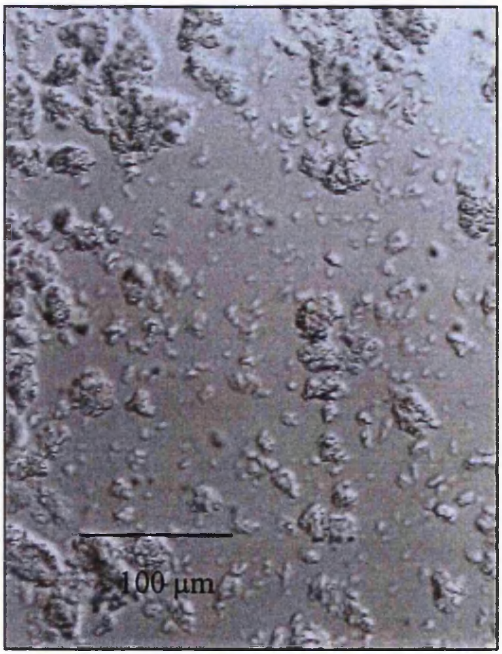


Fig. 4.39 (left): Bentone + Silicone Fluid sample processed using Double screen Silverson homogeniser @ 50°C (x 20 DIC)

Fig. 4.40 (right): Bentone 38 + Silicone Fluid sample processed using HP homogeniser Rannie @ 50°C (x 20 DIC)

Process Equipment	**Shear rate**	**Viscosity/cP** **TA @ 10 rpm**	**Visual Comments**
Heidolph Stirrer	Low	100	No structuring – immediate sedimentation
Lab Scale L4R Silverson Homogeniser	Medium	120	No structuring – immediate sedimentation
Pilot Plant Double Screen Silverson Homogeniser	Medium	130	No structuring – immediate sedimentation
APV Minilab Rannie Homogeniser	Very High	>500,000 26,000 * (* TC @ 10rpm)	Highly viscous, stable gel. No syneresis observed

Table 4.1 : Summary chart of viscosity measurements and visual observations of samples manufactured at 50°C over a range of shear rates

From these results, it can be concluded that at low and medium shear rates, temperature has no effect on increasing product viscosity through melting the quaternary ammonium compound to aid slippage of particles and improving delamination.

Conversely, the viscosity of gel made using the High Pressure Rannie Homogeniser (2 x 1000 bar) pass at high temperature had a bulk viscosity of >500,000 cP compared to the viscosity of 15,000 cP when the mixture is processed at room temperature. These data show that elevated temperature processing has a very significant effect when combined with mechanical energy. The force of shear in the high-pressure homogeniser is extensional flow. This means that effectively as the particles pass through the homogeniser head, the particles are dragged apart in a lateral direction. The molten quaternary on the surface of the clay could act as a lubricant enabling the platelets to glide across each other and disperse more effectively. Once dispersed and the mixture cools back down to room temperature, the quaternary would recrystallise back to its semi-solid phase.

The micrograph would indicate that on cooling the particles do not re-agglomerate back to their original agglomerate dimensions. Some reagglomeration would inevitably occur since platelets in close proximity would be drawn together by their attractive van der Waals forces of attraction or electrostatic charging. At the same time, a degree of repulsion may also occur through steric hindrance and volume filling of numerous individual or minute agglomerates and the possible presence of an electric double layer.

To conclude, a very stable gel network with a high viscosity was achievable without the aid of a polar activator through utilising the energy provided through a combination of extensional flow at very high shear rates and thermal energy above the phase transition of the quaternary ammonium compound.

4.8 The Microstructure of Bentone 38 Gels

4.8.1 Forward

It is assumed that the gel that is formed through high shear processes is composed of a network of primary clay particles or platelets of dimensions in the region of 1μm x 1μm x 0.001μm. Despite the face surfaces of the clay being coated with a quaternary ammonium compound, reference is made to the electrically charged negative face, positive edge 'house of cards' structure hypothesis (van Olphen, 1986) that has been suggested for hydrophilic clay structures. Currently, there is no clear evidence that the microstructure of an organoclay does exhibit a 'house of cards' structure. In fact there is minimal evidence that a house of cards structure exists for hydrophilic clay gels. It is possible that electric double layer, van der Waals forces, steric and space filling factors are likely contributors to the resulting structure of an organoclay gel. It is therefore possible to state that very little prior knowledge as to the microstructure of an organoclay has been reported prior to this investigation. The aim of this study is to investigate the microstructure of Bentone 38 gel through electron microscopy. Both standard Scanning Electron Microscopy (SEM) and cryogenic SEM was applied.

4.8.2 SEM Test Samples and Procedures

Samples of the standard Bentone, Silicone and Propylene Carbonate formulation were used in this study. These were processed using the Rannie Minilab homogeniser (2 passes @1000 bar) to create a viscous gel. As a comparison, samples of dry Bentone clay were also analysed to visualise the Bentone clay in its original state.

Scanning was carried out using a JEOL 840 Scanning Electron Microscope (University of Minnesota, IL, US courtesy of Dr P Carew). The microscope has a magnification range of 10x to 300000x. Cryo-SEM samples were prepared using a dedicated cold system to enable fracture, sublimation and gold coating of liquid ethane vitrified gels.

4.9 Results

4.9.1 SEM Images

Figures 4.41 and 4.42 show micrographs of the raw material Bentone 38 in dry form. This serves as a benchmark in order to establish the form of the organoclay. These images are depicting the SEM images. The images show evidence that Bentone 38 platelets are agglomerated with a compact flake-like microstructure. The numerous morphologies on the surface of the agglomerates indicating that primary particles are completely random in size. Rather than the layer-like stacks as described in many of the texts, the microstructure of the Bentone 38 agglomerates indicates the platelets wrap around neighbouring platelets to form a rounded agglomerate that could be described as boulders. It is apparent from Figure 4.42 that Bentone 38 (dry) granules are polydisperse, ranging from many hundreds of microns to less than 10 microns.

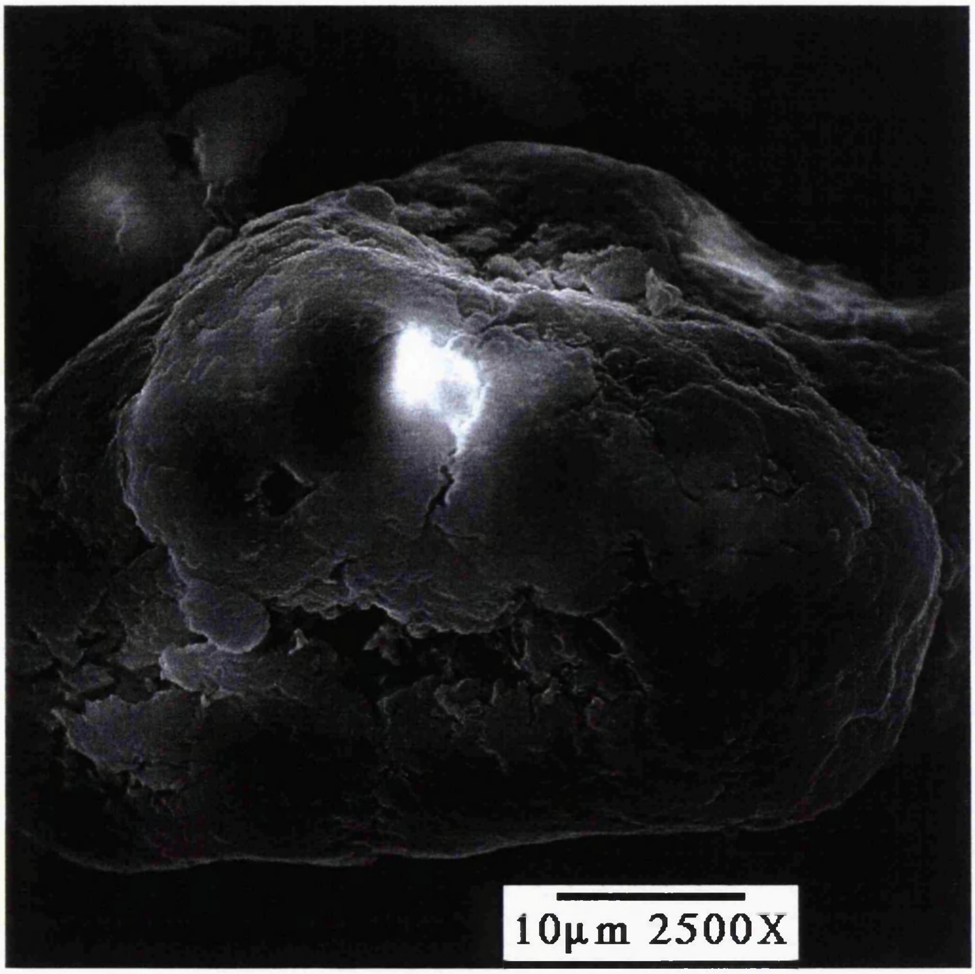


Figure 4.41 : SEM Image of a particle of Bentone 38

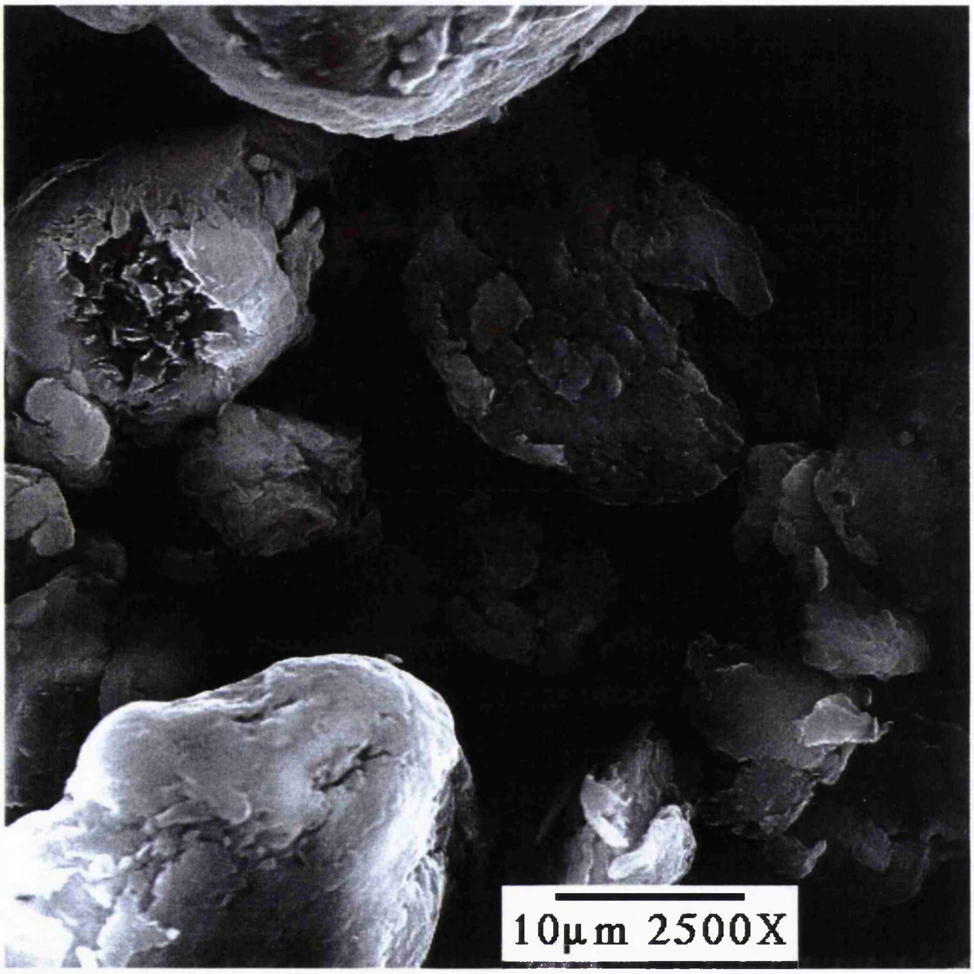


Figure 4.42 : SEM image of Bentone 38

4.9.2 Cryo-SEM Images

Figures 4.43 and 4.44 show the micrographs of the Cryo-SEM sample of the organoclay dispersed using the Rannie Homogeniser. Formulations with and without propylene carbonate were imaged and no difference between the gels could be detected. The images show the micrographs for the formulations without propylene carbonate. Here the images show the sublimed fracture face which has had the surface oil sublimed. This provides strong indication of the microstructure of the organoclay gel within the limits of using this technique. The image shows the surface permeated by channels between two concentrated areas of agglomerated clay. Figure 4.43 shows two levels of porosity. The primary particles are agglomerated in open, oil containing structures approximately 10 microns across. These agglomerates are separated by channels, 2-3 microns wide, that appear as voids on the micrograph. These are indicative of oil-rich regions. Figure 4.44 shows that these channels can inter-link and form fractures which extend to over hundreds of microns and therefore provide a route to oil drainage and instability of the gel as a whole.

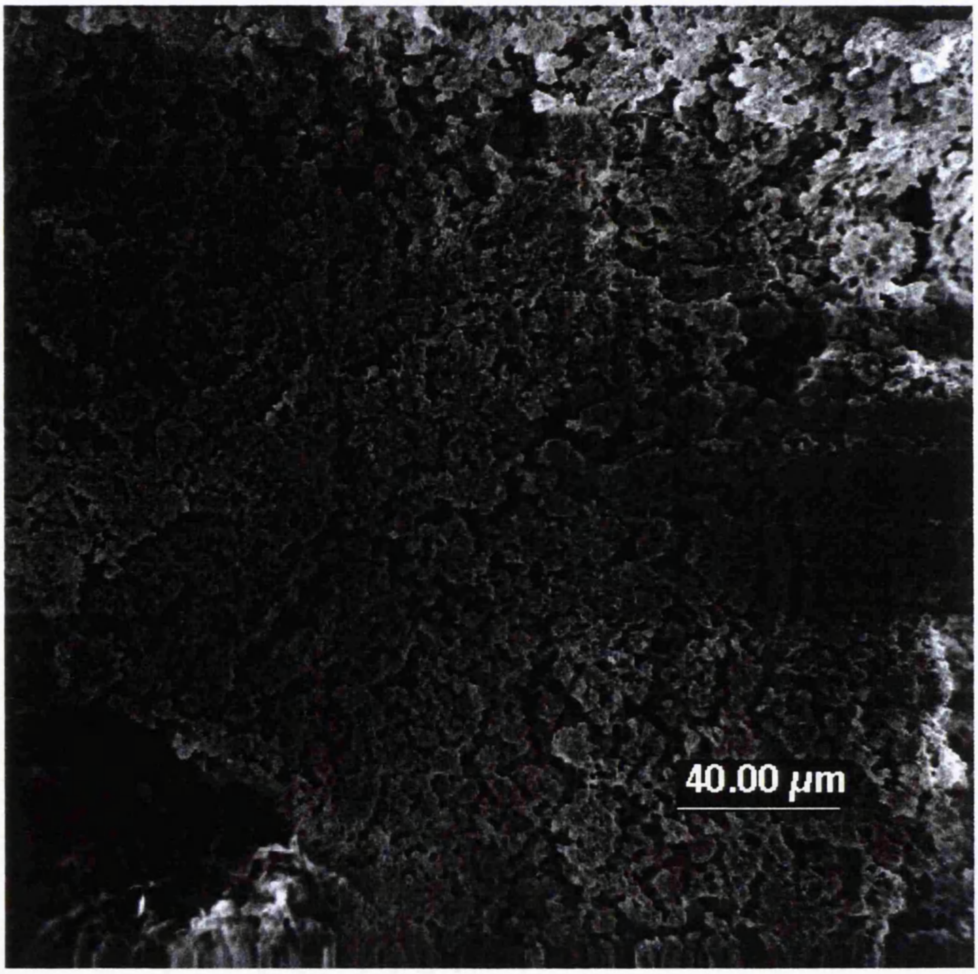


Figure 4.43 : Cryo-SEM image of Bentone 38 Gel (Bentone 38 and Silicone Fluid)

The micrographs clearly show that the microstructure of the gel formed does not represent the ‘house of cards’ structure that is frequently quoted for clays. There is no apparent formal face to face, edge to edge or edge to face linkages. Rather the microstructure would appear to be a random organisation of particles that form a steric and volume filling arrangement. The platelets, once prised apart from their agglomerate arrangement seek to fill the space by volume. From the images it does not seem likely that once this open network has been formed, that re-agglomeration through re-alignment of crystals would ever enable the platelets to reform to their original Bentone 38 clusters.

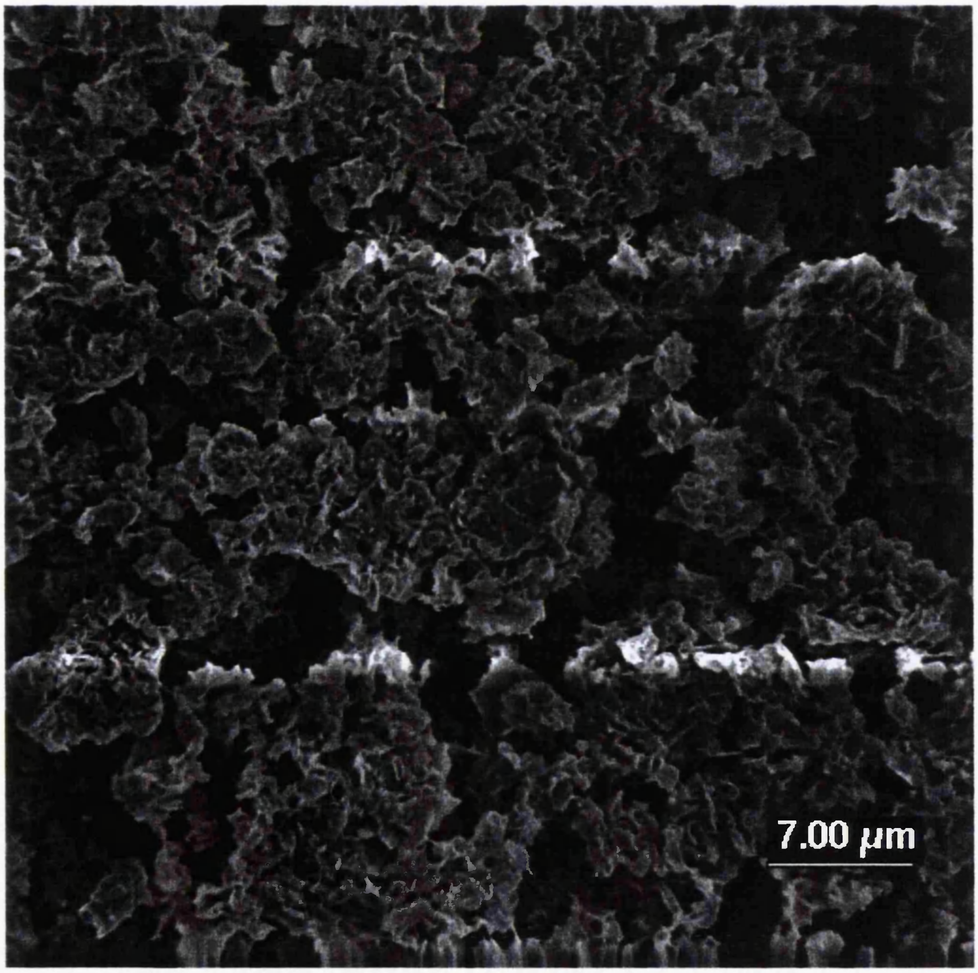


Figure 4.44 : High magnification Cryo-SEM image of Bentone 38 gel

(Bentone 38 and Silicone Fluid)

4.9.3 Comments Regarding Microstructure of Bentone 38 Gel

The microstructure of the Bentone 38 gel could be described as analogous to a sponge. The open network of the Bentone platelets would create capillary forces that trap or 'soak up' the silicone fluid and thus the transformation of the liquid/solid form observed under low shear being transformed to a stable gel-like consistency. With this view in mind, compression of the network would result in silicone leakage as the weak bonding between the platelets would be disrupted and the structure would partially collapse just as water escapes from a sponge when it is squeezed. This would account for the observation of syneresis of silicone. Unlike a sponge however, the network would be unlikely to reform as the weak attractive forces would be broken and compression would create a new network that had been compacted to a certain degree and new attractive forces would exist.

Provided the network is fully dispersed and there is sufficient clay in the formulation, the silicone fluid would be trapped within this network to form a stable gel. Insufficient network formation where agglomerates are only partially dispersed would lead to zones of greater voids between particles and thus silicone fluid would not be entrapped though capillary forces. This again would lead to instability and syneresis of silicone fluid.

4.10 Summary

The results of the mechanical and thermal studies indicate that in order to reach the equivalent microstructure of a gel as that when polar activator is present, extremely high shear forces of extensional flow are required to over come the attractive forces that hold agglomerates tightly together. The results also have shown that by merely heating the Bentone 38 to above the melting point of the quaternary ammonium compound on the surface of clay does not aid dispersion unless lateral shear is applied. When lateral shear is applied to a system at elevated temperature, the stability of the gel is equivalent to one that has been manufactured with a polar activator.

At ambient temperature, fairly robust gel may be manufactured through mechanical energy alone, however, repeated shear passes at extreme pressures is required and the stability of the structure is not as rigid as when polar activator is present.

The electron microscopy images give an insight to the microstructure of a gelled system. The microstructure appears to be a random dispersion of platelets, varying in size and dimension. There appears to be no formal structures e.g. edge to face, face to face or edge to edge interactions. Between the platelets lie two sized channels, the larger seemingly would be a result of an open network of platelets forming agglomerates and minute channels where silicone fluid is believed to lie trapped though capillary forces. The images of the microstructure provide a visual measure to explain the gel-like consistency achievable through a combination of mechanical and thermal and/or chemical energies.

CHAPTER FIVE

X-RAY DIFFRACTION

5.1 Introduction

X-ray diffraction (XRD) is used to determine the structure of materials at the molecular level. Its most common application is to determine the position of atoms in crystals. The technique yields the position of chemically linked atoms in molecules and thereby determines the structure. The technique also provides a rapid and simple method for determining unknown substances by comparing diffraction patterns to standard reference patterns and therefore is frequently used as an analytical identification tool. Advances in the technology have enabled determination of the principles of crystal chemistry but its application is also used in a much wider field e.g. structure of vitamins, haemoglobin and DNA.

Historically, X-ray diffraction was instrumental in providing the evidence that clay minerals were composed of specific minerals and thus enabling definitive structures for clay minerals to be identified e.g. montmorillonite, kaolinite and the more complex mixed layer minerals. The knowledge imparted through the understanding of clay minerals by X-ray diffraction leads to research into numerous practical applications in agriculture, engineering and industry. Examples of the application of XRD with clay minerals include drilling muds, catalysts for cracking petroleum and, in particular, organo-modified montmorillonite.

In more recent years, X-ray patterns have provided the insight to reactions on the surfaces of clay minerals. In particular, changes on the surfaces of clays of the organic matter through charge and defects can be identified through X-ray diffraction patterns.

XRD has been used as a technique to study the basal spacings for Bentone 38 (as described in Chapter One). The increase in basal spacing was correlated to the measure of degree of dispersion.

It is these changes to the organic substrate, dimethyl dialkyl quaternary ammonium compound, on the surface of vermiculite clay that is of interest in this series of work. The aim of the study was to investigate the swelling behaviour of a single crystal of a model vermiculite clay that had been organically modified in the presence of polar propylene carbonate and non-polar silicone fluid over a range of temperatures by determining the basal spacing between the crystal layers. The basal spacing of a crystal in the absence of polar activator or solvent was also analysed to serve as a control and to provide a benchmark. This crystal was also analysed at elevated temperature to investigate whether thermal energy contributes to swelling. The XRD technique to measure basal spacings is known as Low Angle XRD and scans the crystal between 0 and $35^{\circ}2\theta$.

A model clay was used since the diffractometer available for experimental work was a single crystal monochromator. The size of the crystal had to be of sufficient dimensions in order to be mounted into the sample chamber therefore it was not possible to evaluate Bentone 38 crystals that are too small to be analysed on this instrument. The time that was scheduled to this equipment (by agreement through Oxford University) did not allow for major modifications to retrospectively design a powder sample chamber to enable analysis of Bentone 38. The objective of this stage of study was to determine whether polar activators had a significant effect on the swelling of an organoclay. It was decided that a model vermiculite that has a similar chemical structure to Bentone clay would be coated with the cationic quaternary ammonium compound used in Bentone 38 manufacture and would be a representative model system. The X-ray diffractometer had been designed to enable swelling over different temperatures to be evaluated and therefore the second part of this investigation was to determine whether temperature had an influence on the swelling properties of organoclays.

5.2 The X-ray Diffractometer

5.2.1 Introduction

In order to generate reliable data it is essential to comprehend the functions of the diffractor components. Secondly, it is important to have a thorough understanding of alignment techniques.

The diffractometer used in this plan of work was a Philips X-ray Diffractometer (Physical and Theoretical Laboratory, Oxford University). A digital image of the instrument may be found in Appendix 5.1. The X-Ray Diffractometer is a single-crystal monochromator that is essentially a small spectrometer using a curved graphite crystal placed just in front of the detector. This is configured so that a prominent set of spacings of the graphite crystal diffracts the K-α part of the X-ray beam into the detector.

K-α is the radiation that is formed as a result of electrons that fall from the outer orbitals (L shell) to the inner orbital (K-shell) that have vacancies following bombardment of the target metal (Cu). K-β radiation is formed from electrons that originate from the outer orbitals (M and N shells) and is usually filtered out using a Nickel filter.

A description of the main components of the diffractometer follows with a more detailed explanation of the optical assembly. The alignment of the diffractometer is then described.

5.2.2 Components of X-ray Diffractometer

5.2.2.1 Basic Components

- **Generator** (PW1730) is the control unit that supplies the X-ray tube with between 20 and 60 watts and up to a maximum of 2Kw per tube. It is also used to monitor the flow rate of the water cooling system that is required to maintain the tubes in a cool environment. The current and voltage of the X-ray tube are controlled from the panel of the generator. The current (measured in milliamps, mA) heats the filament of the X-ray tube. The more current, the larger the number of electrons available to be pulled across the gap to strike the sample. Voltage is transformed from domestic supply levels (220V) to voltages from 5 to 50kV which are used to accelerate electrons across the gap in the X-ray tube. Current and Voltage must be absolutely constant when comparing intensities of peaks between samples. These are set to 30W and 50mA on the instrument used for this series of experiments.

- **Water Cooling System** (Alfa-Laval PC03/HD) is a closed circuit system comprised of normal vapour pressure refrigeration. It absorbs heat from process water generated by the X-ray tube and dissipates it to ambient air. A closed circuit system has the advantage of maintaining flow rate and constant water temperature and reduces the amount of contamination that would otherwise reduce the flow rate to the X-ray tubes.

- **X-ray Tube Tower House** (PW2213/20) is a 1500W Cu-fine focus tube producing a line source of X-ray radiation of a dimension 0.4mm wide by 8mm high. It is mounted on a horizontal steel table and can be adjusted for vertical height and rotated in the plane of the table. Copper tubes are the most common in X-ray diffraction generating beams of 1.54 Å however, cobalt tubes are being chosen more frequently primarily for wavelength (1.79 Å) since they shift the low angle peaks to slightly higher angles.

- **Goniometer** (PW1380/70) is the device that measures the angle of diffraction and is mounted securely to the steel table and comprises a stepping motor driven by a software interface system allowing minimum incremental steps of 0.005 and 0.0025 in degrees of 2θ and θ respectively.

- **Monochromating System.** An AMR focusing monochromator is mounted onto the detector arm of the diffractometer and comprises a curved graphite crystal. It is adjusted to select from the diffracted beam, the dominant Cu K-α wavelength from the X-ray tube target while rejecting other wavelengths.

- **Detector** (PW1964/60) is a scintillation detector consisting of a NaI crystal and a photomultiplier tube. It is fixed at the end of the detector arm. The detector is sometimes termed a quantum counter that catches and reacts to the diffracted beam and short-wavelength, ionising radiation. The detector responds to a range of voltages that are characteristic to the model and are determined by setting the detector at an angular position and adjusting the voltage and current so that the detector receives a diffractive beam of moderate strength.

5.2.2.2 Optical Assembly

The optical arrangement is normal reflection geometry for single crystal XRD. The optical assembly for the X-ray diffractometer is shown in Figure 5.1.

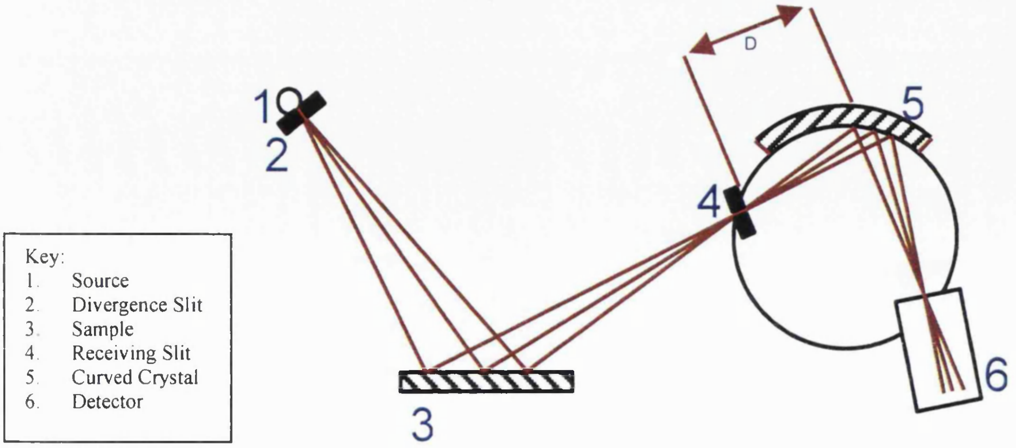


Figure 5.1 : Diagram of Optical Assembly

The centre of the beam is at a height 104.5mm above the goniometer, positioned to coincide with the centre of the monochromating crystal. The emerging beam passes through a shutter opening into a Soller slit and a 1° divergence slit before striking the sample. These slits collimate, limit and direct the high-resolution beam. The slit at the source of radiation limits equatorial beam divergence. The scattered beam passes through a second slit (receiving slit, limiting axial beam divergence), positioned at a distance from the goniometer that is equal to that between the X-ray tube target focal spot and the goniometer axis, and is reflected off the graphite monochromating crystal.

The distance (D) between the receiving slit and monochromating crystal is determined from the focusing condition:

d = crystal spacing
R = radius
λ = wavelength

$$D = \frac{R\lambda}{2d}$$

Equation 5.1

The focused beam is then allowed to reach the detector via a nickel filter without any further monochromation.

Nickel filters are used in the case of CuK-α radiation to filter out and eliminate the β contribution. In theory, by using a monochromating crystal, a β filter is not essential. However, the instrument at Oxford University includes the nickel filter in its set up.

Monochromation is improved by using a crystalline monochromator. If the crystal is curved, focusing of CuK-α radiation that result, enables beams of greater divergence to be used and therefore allows greater intensities to be achieved.

In choosing a suitable crystal, the following must be applied :

- Reflective plane must have high structure factor and low Bragg angle (this minimises the loss of intensity to polarisation)
- Crystal should be free of polycrystallinity or gross imperfections that could result in multiple reflections and an increased background.
- Crystal should be sufficiently robust to withstand prolonged exposure to X-rays and atmosphere without deterioration.

Such crystals that are suitable for this application include quartz, rocksalt and lithium fluoride. The Philips diffractometer uses the pseudo single crystal of graphite that has low planar mosaic spread and has XRD efficiencies of greater than any known material making it the optimum choice of XRD monochromation

A Soller slit consists of two, closely parallel metal plates that are highly absorbing. They are placed normal to the aperture of the receiving slit. Soller slits direct the plane of the X-ray beams while the divergence slit controls the area of the sample exposed to the X-ray beam. The receiving slit is situated on the diffractometer circle in front of the single crystal monochromator and controls peak sharpness and resolution. The reflected rays focus approximately on the diffractometer circle while the receiving slit eliminates any rays that are scattered.

The source of the X-rays, or the tube, is also positioned on the diffractometer circle so that the distance from the tube to the sample is equal to the distance from the sample to the receiving slit. Both distances are therefore radii of the diffractometer circle.

The sample is mounted onto the sample holder and positioned into the sample chamber such that the principal axis is parallel with one of the goniometer axes. The sample chamber is fitted with a water jacket that allows a constant temperature to be maintained via a Haake water bath. It also enables the sample to be heated or cooled accordingly. The beam is directed to the sample through a mylar window.

The Philips diffractometer is designed such that the sample remains fixed in the centre of the goniometer and the tube and the detector rotate through the same angular value θ, one clockwise and the other anti-clockwise.

5.2.2.3 Alignment of Instrument

Prior to any experimentation, it is critical to mechanically align the instrument. This is to ensure that precise and accurate data is generated. Primarily, the radiation beam must be aligned with the goniometer axis by replacing the inner chamber of the goniometer with a standard measuring chamber. The instrument is calibrated by mounting a fluorescent disc in the goniometer axis and generating a low intensity X-ray beam. By viewing the fluorescent disc through a window on the top of the goniometer, minor adjustments are made to the relative positions of the goniometer and the source tube until the beam centrally strikes the disc. Smaller divergence slits that produce a very fine line source are used in this operation to enable very accurate adjustment. Testing of alignment using a reference specimen is also performed using commercially available materials e.g. quartz. Alignment of the instrument needs only to be performed periodically, and in general is checked on monthly intervals.

5.2.2.4 Alignment of Crystal

It is equally critical to ensure that the crystal under observation is also aligned in the instrument. Alignment of the crystal is performed each time a major parameter is changed e.g. when the temperature setting is altered, addition of a solvent or a new crystal is used. The beam must be focused accurately on the crystal to generate counts of a significant intensity in order to ensure clear, ‘clean’ peaks.

The crystal is mounted onto the sample holder and positioned in the sample chamber such that the principal axis is parallel to one of the goniometer axes. Using the software programme MCCM, the detector arm is moved to the zero position. The sample is adjusted manually by eye so that it is parallel with the detector. Ensuring that θ and 2θ are coupled; a fast scan is made of the lower region to locate a peak. The relatively large mosaic spread ($4^{o} - 8^{o}$) of the crystal enables alignment initially by eye is sufficient to obtain a peak.

The plot in Figure 5.2 shows a typical mosaic spread for the crystal. The detector is then moved to the position that corresponds to the maximum intensity on the plot and θ and 2θ are uncoupled. The sample itself is now rotated to find its optimum position (θ 0 angle). Once this is located the two movements are re-coupled and a diffraction scan is repeated. This procedure is repeated until a satisfactory intensity is achieved. Minor adjustments to the position and height of the sample may be made manually to the goniometer arc settings to improve intensity.

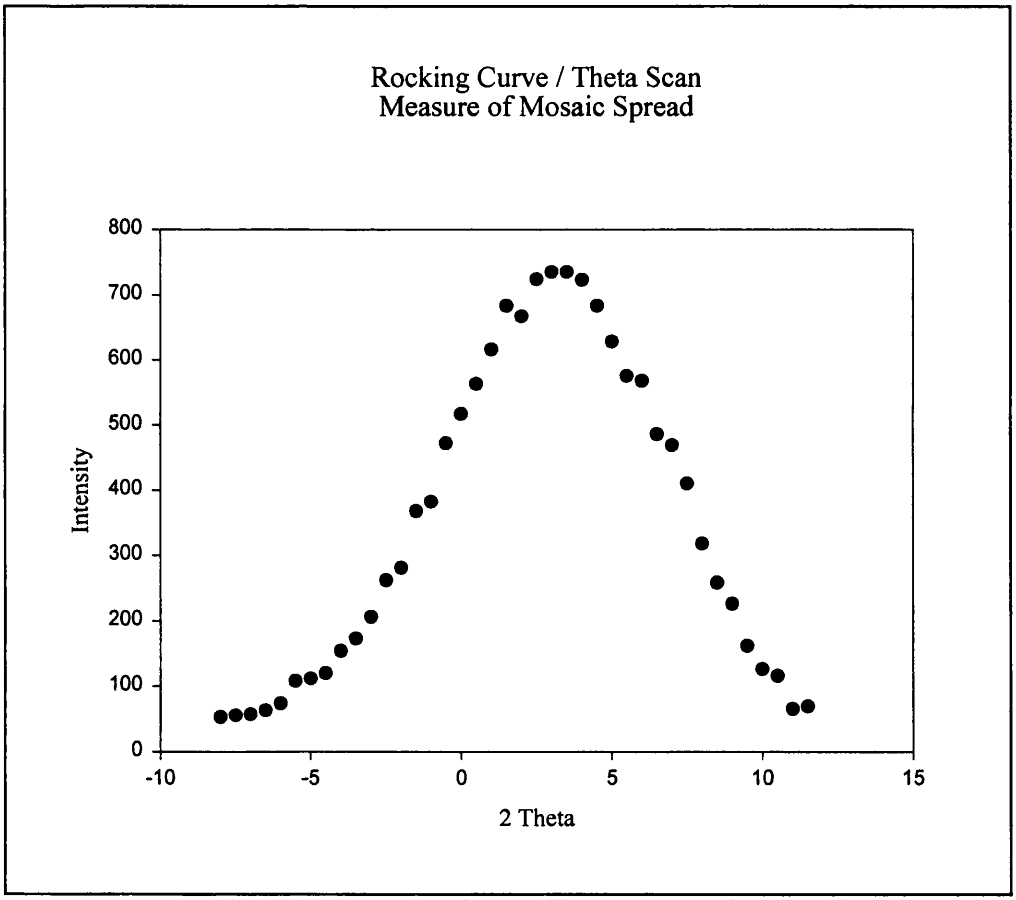


Figure 5.2 : XRD Plot to Illustrate Mosaic Spread

5.3 Experimental Details

5.3.1 Model Clay

The model crystal, Eucatex vermiculite (Brazil) of dimensions approximately $50mm^2$ and 1 mm thick was used in this study. Eucatex Vermiculite has the general formula :

$[(Si_{6.22}Al_{1.7})^{4+}(Mg_{4.95}Al_{0.15}Fe_{0.61}Ti_{0.08}Mn_{0.01})^{6+}]O_{20}(OH)_4.Na_{1.4}$

Eucatex Vermiculite was selected as a suitable model clay for Bentone 38 since it has a similar basic structure to montmorillonite and has a net negative surface charge enabling cationic exchange. The advantage of using the model clay is primarily the dimensions of the crystals enable single crystals to be studied. By exchanging the sodium ions on the face surfaces of the vermiculite for dimethyl dialkyl ammonium chloride, the Eucatex crystals serve as a good model for Bentone 38.

The Eucatex Vermilculite was supplied in its homoionic form having previously been prepared using the following procedure (Garrett and Walker, 1962). The crystals were washed and soaked with a 1M NaCl solution (50°C, 6 months) to yield a pure sodium vermiculite. To be confident of the completeness of the exchange, the regularity of the *c*-axis spacing on the XRD pattern (14.9Å for the sodium form) was checked. The crystals used in this study were supplied (PCL, Oxford University) in the pure sodium vermiculite form.

To prepare the Eucatex Vermiculite in an organically modified form, the sodium-rich Eucatex clay was soaked in 0.1M dimethyl dihydrogenated tallow quaternary chloride solution (Genamin DSAC, Clariant, CAS No 61789-80-8) (50°C, two weeks), washed with doionised water and dried in a dessicator. Purity of the sample was confirmed by X-ray diffraction, the *c*-axis spacing now being ~40Å. The crystals were stored in the dessicator until required. The solvents used in the experiments were Silicone Fluid 1465 fluid (Dow Corning) and Propylene Carbonate (Honeywell and Stein).

5.3.2 Sample Preparation

The diffraction experiments were carried out on the Philips Diffractometer (Oxford University). The incident wavelength was 1.54Å. A dry crystal of uniform appearance of dimensions approximately 6 x 8 mm^2 was chosen for each experiment. Small holes were made at the top and bottom of the crystal using a fine needle and cotton was threaded through each hole. The crystal was then tied to the sample mount as shown in Figure 5.3.

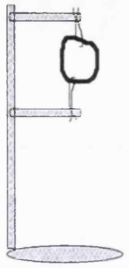


Figure 5.3 : Diagram of Crystal Mount for X-Ray Diffractometer

A small piece of double-sided tape was fixed to the bottom of the mount and the sample was placed into the sample chamber positioning the crystal opposite the mylar window. Solvent was added to the chamber by means of a micro-pipette. The base of the chamber was flooded with solvent and the sample was washed with solvent by pipetting excess solvent over the crystal repeatedly. The chamber was then sealed to maintain a solvent saturated environment.

Temperature was set at 25°C as standard procedure and controlled by means of a Haake water bath that recirculated around the sample block. For samples that required elevated temperatures, the water bath was programmed to heat to the required temperature and the sample allowed to equilibrate overnight. The sample was then aligned as described in the procedure earlier. Once a suitable intensity level had been achieved the sample was then scanned from 0-35 2θ at intervals of 0.05 seconds using a specialised MCCM computer software programme. Crystals were replaced with each solvent system.

5.4 Interpretation of XRD Plots

5.4.1 Description of the Characteristics of XRD plots

Each clay mineral diffraction pattern contains a good deal of character. This character is manifested by the peak's position, intensity, shape and breadth.

5.4.1.1 Peak Position

Peak position is determined by the Bragg Law ($n\lambda = 2d\sin\theta$). At low diffraction angles (values of 40° 2θ or less), basal spacings are equidistant. Measurements of the peak positions are conventionally measured with a ruler. In this study, for greater accuracy, raw data were used to identify maxima of peaks and to calculate the difference between 2θ. By substituting this value and the wavelength value ($\lambda = 1.54$ for Cu) into the Bragg equation, it is possible to identify the basal spacing (*d*) between the crystal layers. An explanation of the Bragg Law follows:

- Bragg's Law or the Bragg equation was first worked out by W. L. Bragg in 1912 (Bragg, 1913) and is the most important relation for the use and understanding of X-ray diffraction. It is most commonly written in the form of Equation 5.2

$$2d\sin\theta = n\lambda$$ **Equation 5.2**

d = basal spacing
λ = wavelength
θ = angle at which an X-ray strikes the crystal surface

When considering a single plane of atoms, the rays of the X-ray beam move towards the atoms in phase. The atoms in the plane are stimulated by the incident rays to scatter in all directions. To determine the direction the scattered rays will constructively interfere and form a diffracted beam it is necessary to remember that the reflected rays must be 'in phase' i.e. to be in the same place as the sinusoidal cycling pattern differing by integers of wavelengths.

Figure 5.4 shows a diagram of incident rays R_0 and R'_0 striking atoms A and B at an angle θ. Rays R_x and R_x' are diffracted by an angle θ′ when R_x and R_x' are 'in phase'. When $\theta = \theta'$, AC and BD are the same length and the following relationship may be deduced (Equation 5.3) since both AD and BC are related to AB in the same way.

$$AD - BC = AB\sin\theta - AB\sin\theta = 0$$ **Equation 5.3**

.This shows that there is zero wavelength difference between the incident rays and the reflected rays and therefore the beam is diffracted. Diffraction can occur at any angle in a single row of atoms when the condition θ = θ′ is met.

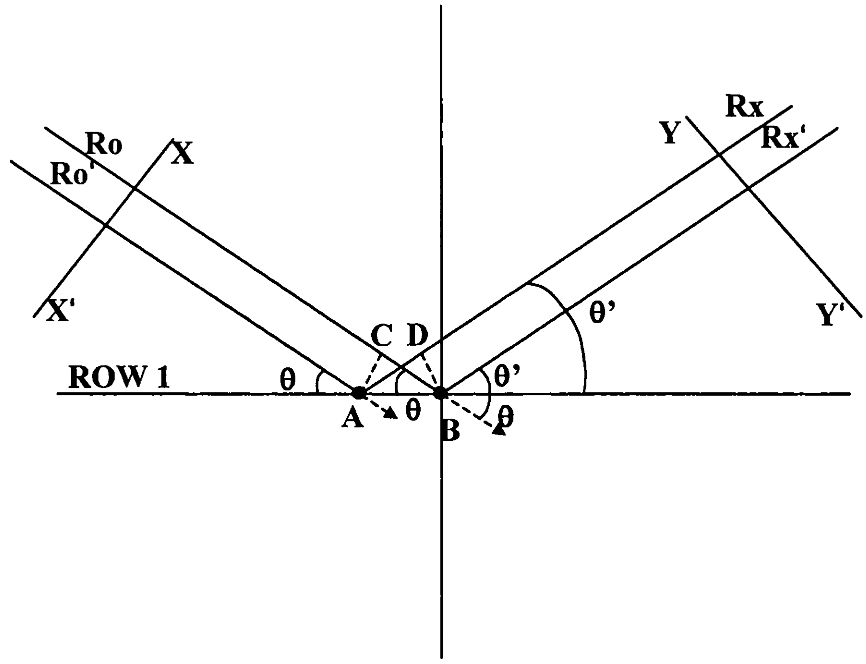


Figure 5.4 : Diffraction from a Single Row of Atoms

To illustrate Bragg's law, it is necessary to consider diffraction from more than one plane of atoms, as experienced in crystalline structures. This is represented in Figure 5.5

Rows 1 and 2 represent two planes of atoms. In order to have a diffracted beam, the rays R_x, R_x' and R_x'' at the wavefront Y - Y′ must be exactly in phase. In order for the rays to be in phase with one another, ray R_x'' must have travelled farther than rays R_x and R_x' and must have a pathlength exactly some whole integer longer. To express this geometrically, the extra distance ray R_o-R_x has travelled is equivalent to FE + EG. This distance must equal some whole wavelength. The two triangles FEB and GEB have a common side EB that is equivalent to the distance between the two planes *d* and angle FBE equals θ. To arrive at the equation that relates the angle of incidence, spacing between rows and the wavelength difference in terms of the wavelength of the incident rays it is necessary to express EB in terms of sin θ and FE and EG in terms of an integral number of wavelengths. Therefore,

$\text{Sin}\ \theta = FE/BE$ **Equation 5.4**

and

$\sin \theta' = EG/BE$ **Equation 5.5**

Therefore, because $\theta = \theta'$

$2BE \sin \theta = FE + EG$ **Equation 5.6**

Substituting $d = BE$ gives

$2d \sin \theta = FE + EG$ **Equation 5.7**

The wavelength difference that must equal some integral number of wavelengths $n\lambda$ is equal to FE + EG so gives the Bragg Equation:

$2d \sin \theta = n\lambda$ **Equation 5.2**

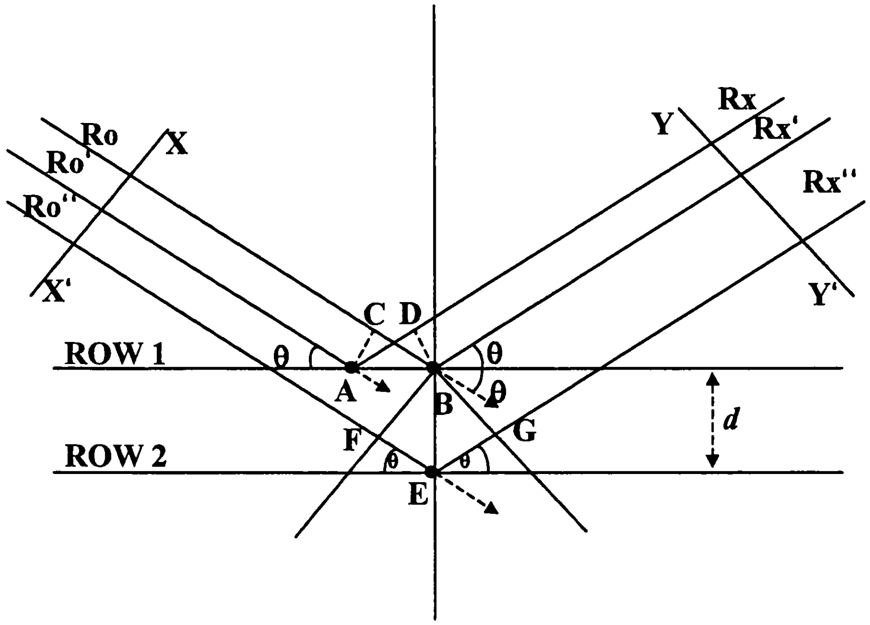


Figure 5.5 : Diagram to show Diffraction from more than One Row of Atoms Illustrating Bragg's Law

Consequently, with the θ data obtained by XRD and using the Bragg equation, it is possible to calculate *d*, the basal spacing between crystal layers and therefore assess swelling potential.

5.4.1.2 Peak Intensity

Peak intensity is controlled by chemical composition and the positions of atoms in the unit cell and the Soller slits on the goniometer. This is where the importance of aligning a crystal as described in the methods is critical. The aim is to ensure that a high intensity is obtained at the low degree 2θ measurements since intensity decays at higher 2θ readings.

5.4.1.3 Peak Breadth

Peak breadth is less important in this study since it is a tool required for identification purposes. Peak breadth is a characteristic pertinent to individual crystals. Peak breadth is inversely proportional to the mean dimension (in Angstroms) normal to the diffracting planes in an optically coherent domain. As such, peak breadth is a tool for qualitative analysis and not in the scope of this study.

5.4.1.4 Peak Shape

The shape of peaks is related to peak breadth and the type of mineral being analysed and therefore is a qualitative tool. For example, thick crystallites of illite clay have characteristically sharp peaks, thin crystals of kaolinite have characteristically broad peaks and non-clay minerals like quartz have very sharp peaks. Again, the shapes of the peaks are not important in this study, since only vermiculite clay is being analysed.

The peaks between $0\text{-}10^{\circ}\ 2\theta$ serve as a reference to ensure that clean peaks are obtained indicating that the crystal is aligned. The distance between these peaks provides information to determine the basal spacing between the crystal layers. It is conventional to expand the axis and replot the data and calculate the peak distances from the fingerprint region ($\sim 20\text{-}35^{\circ}\ 2\theta$). This is depicted on the figures in red, using an expanded Y2 axis measuring intensity.

5.5 Results

5.5.1 Organically modified Eucatex Clay

5.5.1.1 No Solvent (25°C)

The first stage of experiments was to establish the basal spacing for the Eucatex clay that had undergone cationic exchange. Despite numerous attempts of scanning the crystals, it was not possible to obtain a truly 'clean' plot with sharp peaks. Figure 5.6 shows a typical example of one of the better plots obtained. Attempts to calculate the basal spacings from the plots obtained were made. However, there was a significant spread of results and it is not possible to be confident that the readings are reflective of the true spacings. Consequently, the mean spacing has been calculated and is shown in Table 5.1 that gives a summary of the data.

Initially it was thought that perhaps full cationic exchange had not occurred and therefore contamination from sodium ions was being observed. The initial crystals had been soaked at room temperature in the quaternary solution. The initial XRD scans made indicated smaller secondary peaks with approximately 14 Å spacings that confirmed that a quantity of sodium ions were still present. Consequently, further crystals were prepared by soaking the sodium Eucatex crystals in the quaternary ammonium solution at 50°C since it had been established that quaternary ammonium undergoes a phase transition at this temperature. The philosophy behind this was the quaternary ammonium compound would be liquid and thus able to intercalate more easily between the crystal layers and promote a better cationic exchange.

A slight improvement of the clarity of the peaks was observed with this revised soaking method and the secondary peaks were eliminated indicating that full cationic exchange had occurred. Consequently the Eucatex crystals prepared at elevated temperature were used for all further experiments.

Secondly, it can only be assumed that an even exchange of cationic material has occurred and that water is present in minimal quantities. It is clear from the previous electrophoretic and surface force measurement studies that water has a great affinity for the surface of clay and therefore it is feasible that the crystal had already undergone a certain degree of swelling. Water may not be present in equal quantities in all layers, and therefore could account for why regular basal spacings were not measured.

It is noted that the peaks are not clean, sharp peaks. This is most likely a characteristic of impurities in the quaternary ammonium since it is a commercial grade of compound and had not undergone any purification through recrystallisation. It was a conscious decision not to purify the organic material in order to replicate the coating on Bentone 38.

The results of the calculations for *d* spacings are given in Table 5.1. The overall mean of basal spacing for organically modified Eucatex clay was 41.33Å with a standard deviation of 2.36 that illustrates the diversity of results.

5.5.1.2 No Solvent (50°C)

Figure 5.7 shows a representative plot of the coated Eucatex clay run at 50°C. The sample was allowed to equilibrate at this temperature in the chamber over night. Repeats of these scans were run concurrently.

It was extremely difficult to obtain good alignment for the dry crystals at elevated temperature and as a result, peak intensities were extremely low. This had a significant effect on the fingerprint region where peaks were masked by noise from the scan and it was impossible to identify clear points to calculate the d-spacings. Consequently the basal spacings were calculated from the lower diffraction angles. The results did however indicate a trend in a slight increase in basal spacing when the clay was heated to 50°C. The results are shown in Table 5.2. The mean basal spacing was calculated to be 43.06 Å and a standard deviation of 0.61. This gave an average increase of approximately 2 Å.

Based on the results taken from High Sensitivity Differential Scanning, it is known that the quaternary ammonium compound undergoes a phase transition between 40-50°C. The increase in basal spacing for the clay run at elevated temperature would suggest that since the hydrocarbon chains of the quaternary compound being liquid would have a certain degree of freedom to reorientate on the surface. It is possible that temperature would also weaken the attractive forces that bind the platelets rigidly together. These two factors combined would suggest that the hydrocarbon chains that would lie in the same plane as the face of the clay platelets have undergone some reorientation to move away from the surface.

5.5.2 Organically Modified Eucatex Clay and Propylene Carbonate

Propylene Carbonate was dosed into the sample chamber using a micro-pipette. It is not possible to immerse the sample since the chamber is not sealed to prevent liquids from leaking into the goniometer. Therefore it was necessary to manually soak the crystal and pipette a few drops of liquid into the bottom of the chamber before sealing. It is presumed that the environment of the chamber had propylene carbonate rich atmosphere. As a precaution against solvent evaporation, the crystal was doused in the late afternoon and allowed to equilibriate overnight and then the chamber was topped up again with propylene carbonate just prior to running the sample. In order to establish consistency numerous repeats of the samples were made and the following scans are representative of the plots for each sample. In addition, a summary of the calculations for basal spacings for each run is given and the overall mean calculated.

5.5.2.1 Propylene Carbonate (25°C)

Figure 5.8 shows a typical plot of the results obtained for the samples that were tested at 25°C. The peaks for the clay tested at 25°C were broad peaks with a lot of noise. It was however possible to identify a distinct pattern of equidistant spacing as represented by the first three peaks and the reflected peaks in the fingerprint region at 24 – 32° 2θ. Once again, intensity was fairly low for these samples since alignment of the crystals was difficult. The data shown in Table 5.3 indicates the variation of basal spacing calculations giving an overall mean spacing of 40.19 Å and a standard deviation of 1.48. Comparing the basal spacings for the samples in the presence of propylene carbonate against the dry samples of clay, it would appear that at 25°C propylene carbonate had not had any significant effect on the swelling properties of clay. It also implies that in order for propylene carbonate to intercalate the layers a secondary effect through mechanical energy or thermal energy would be required.

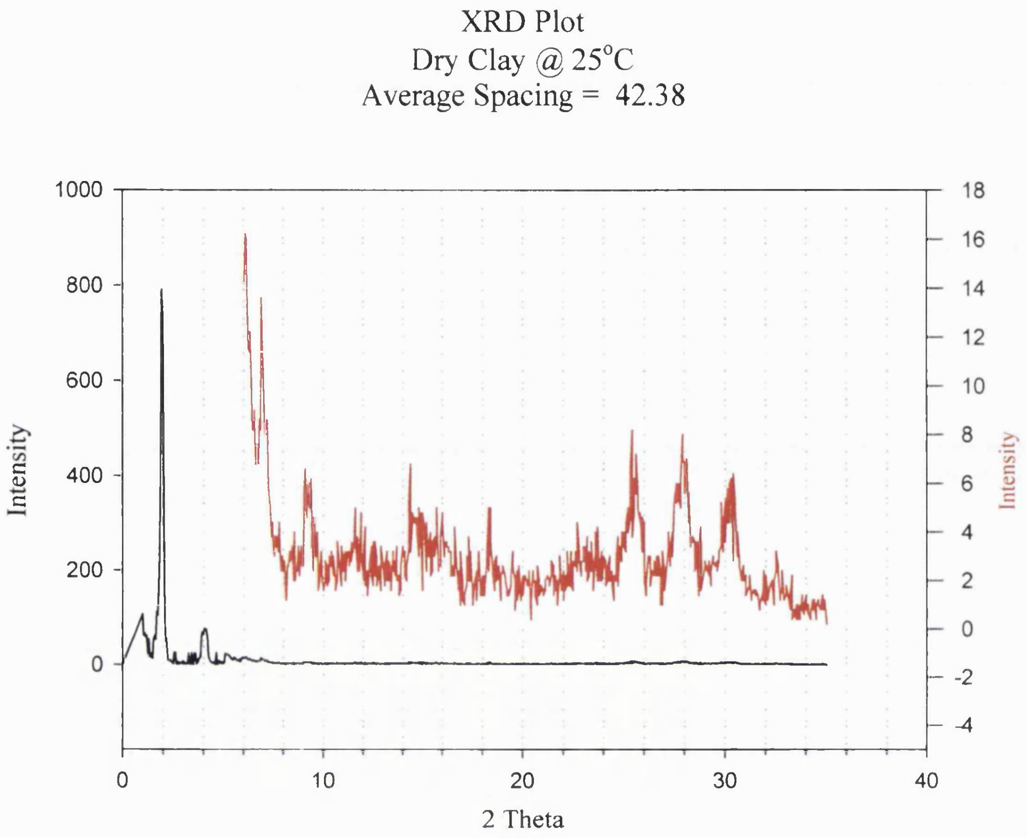
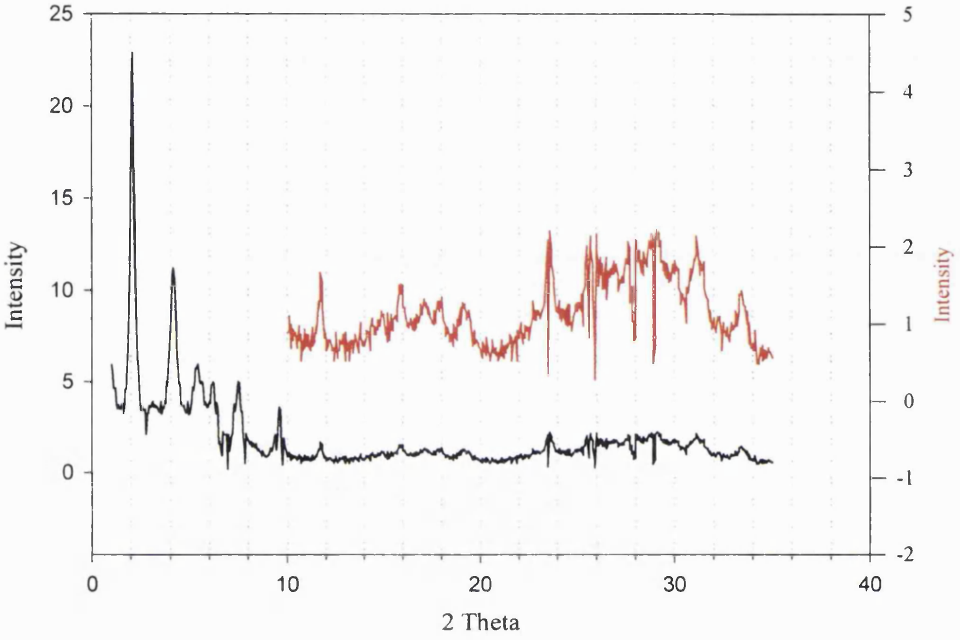


Figure 5.6 : XRD plot for Dry Eucatex clay organically modified with dimethyl dialkyl ammonium chloride. Scanned at 25°C

	1	2	3
Basal Spacing (Å)	42.23	41.00	40.1
	42.02	42.02	42.02
	43.05	44.13	
	35.37		
Mean	40.67	42.38	41.06
Overall Mean	41.33		
s.d.	2.36		

Table 5.1: Basal spacings (Å) of dry clay @ 25°C



XRD Plot
Dry Clay @ 50°C
average spacing 43.05

Figure 5.7 : XRD plot for Dry Eucatex Clay organically modified with dimethyl dialkyl ammonium chloride. Scanned at 50°C

	1	2	3
Basal Spacing (Å)	43.05	43.05	
	43.05	43.05	44.13
	42.02		
Mean	42.71	43.05	44.13
Overall Mean	43.06		
s.d.	0.61		

Table 5.2: Basal spacings (Å)of dry clay @ 50°C

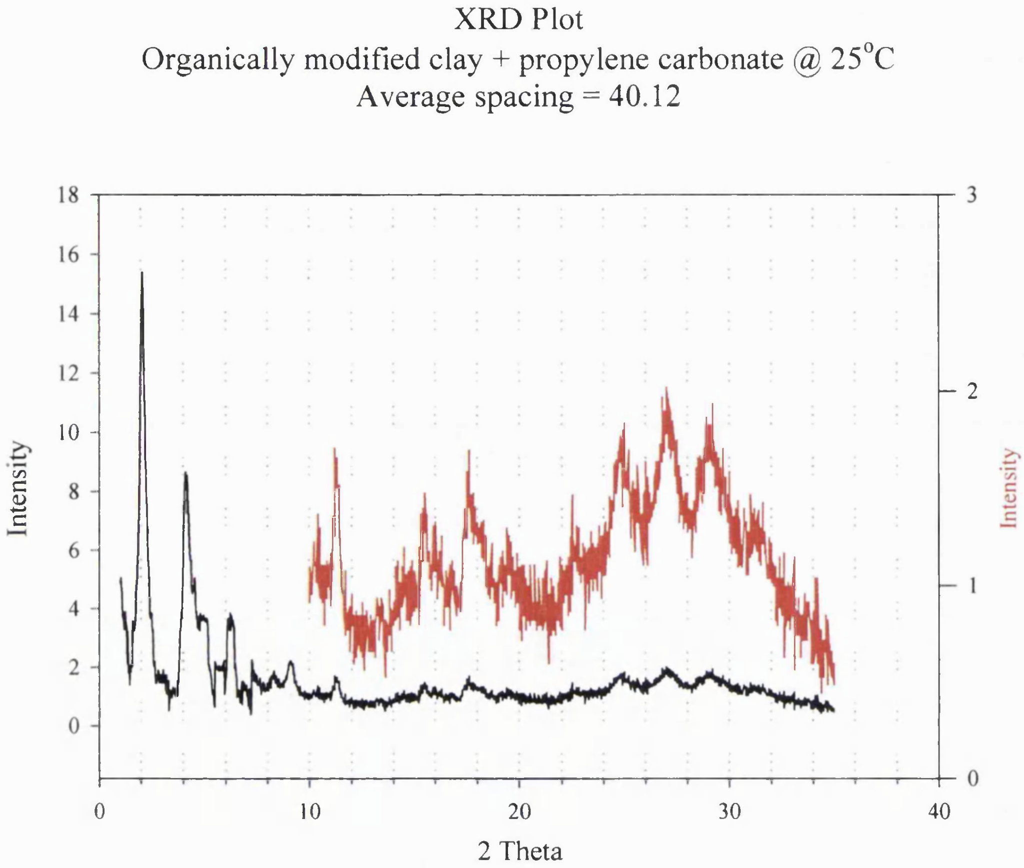


Figure 5.8 : XRD plot for Eucatex clay organically modified with dimethyl dialkyl ammonium chloride and propylene carbonate 25°C

	1	2	3	4	5
Basal Spacings (Å)	42	43.05	40.12	40.12	41.12
	42	42.03	40.12	38.37	38.37
	39	40.11	40.12	42.03	42.03
	40	38.37	40.12		
	38				
	40.1				
	39				
	38				
Mean	39.76	40.89	40.12	40.17	40.51
Overall Mean	40.19				
s.d.	1.48				

Table 5.3: Basal spacings (Å) of organically modified clay and propylene carbonate solvent @ 25°C

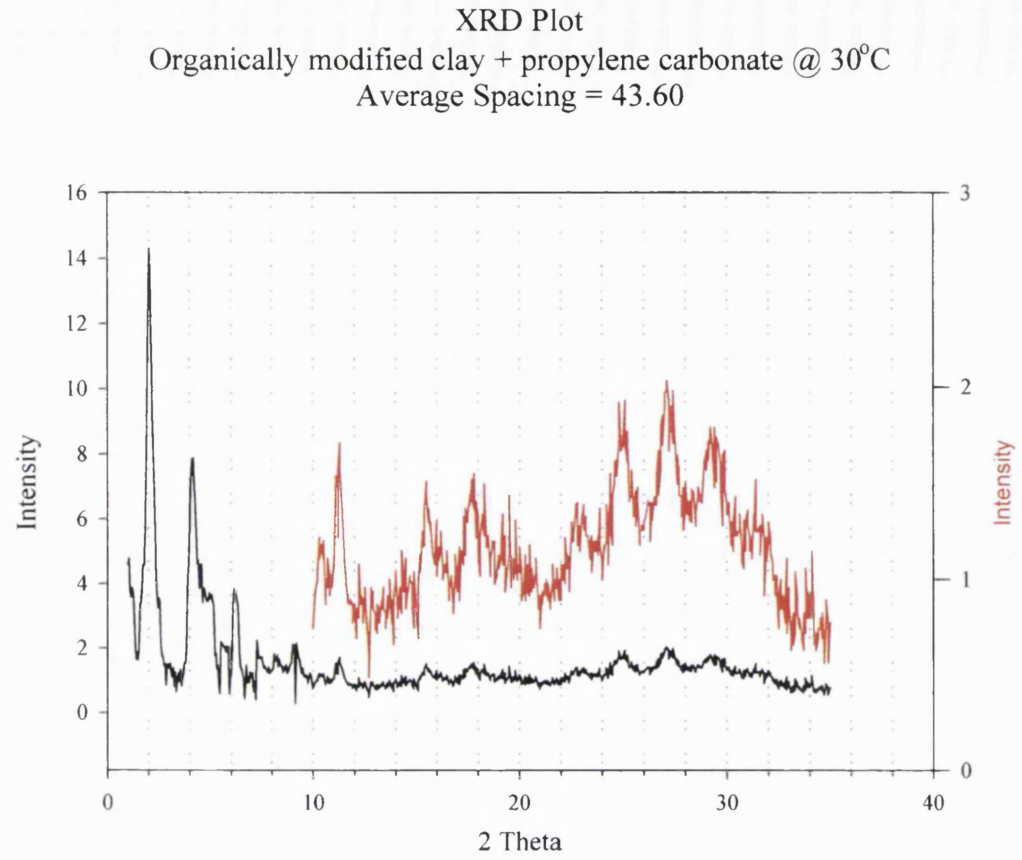


Figure 5.9 : XRD plot of Eucatex clay organically modified with dimethyl dialkyl ammonium chloride and propylene carbonate. Scanned at 30°C

	1	2
Basal Spacings(Å)	42.02	42.02
	44.13	44.13
	44.13	
	44.13	
Mean	43.60	43.08
Overall Mean	44.13	
s.d.	0.63	

Table 5.4 : Basal spacings (Å) of organically modified clay and propylene carbonate @ 30°C

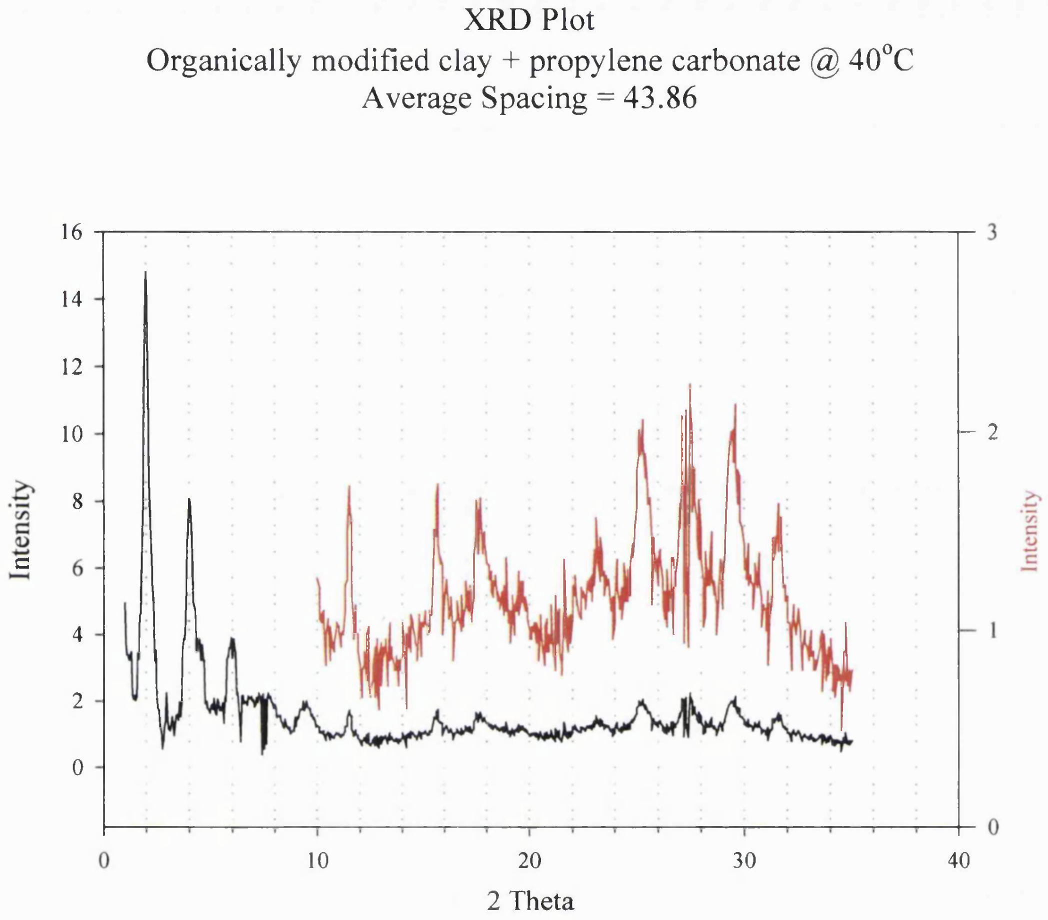


Figure 5.10 : XRD plot of Eucatex clay organically modified with dimethyl dialkyl ammonium chloride and propylene carbonate. Scanned at 40°C

	1	2
Basal Spacings (Å)	44.13	44.13
	43.05	45.23
	44.13	
	44.13	
Mean	43.86	44.68
Overall Mean	43.43	
s.d.	0.99	

Table 5.5 : Basal spacings (Å) of organically modified clay and propylene carbonate @ 40°C

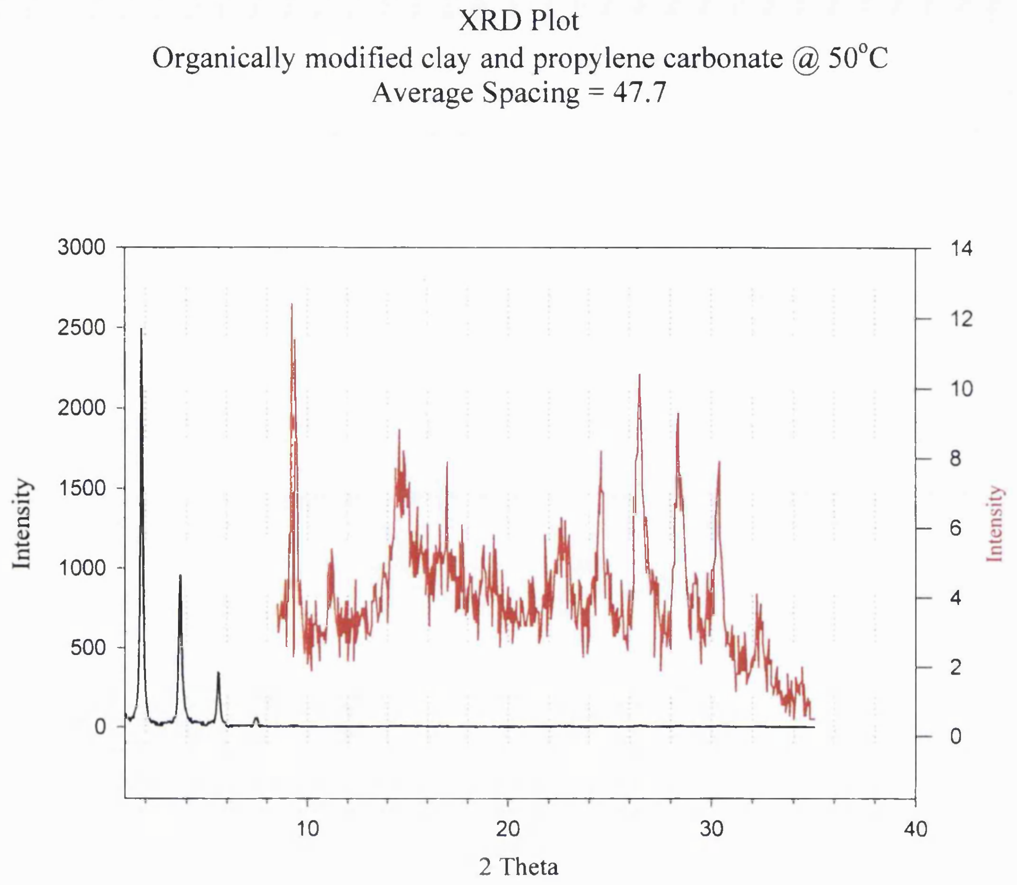


Figure 5.11 : XRD plot of Eucatex clay organically modified with dimethyl dialkyl ammonium chloride and propylene carbonate. Scanned at 50°C

	1	2	3	4	5
Basal Spacings (Å)	47.70	44	51.91	46.45	46.45
	47.70	46.9	44.13	46.45	46.45
	47.70	45.96	49.63	46.45	46.45
	47.70	47.7	44.13	46.45	
	47.70	47.1	42.03	46.45	
	47.70	46.44			
Mean	47.70	46.35	46.37	46.45	46.45
Overall Mean	46.71				
s.d.	1.86				

Table 5.6 : Basal spacings (Å) of organically modified clay and propylene carbonate @ 50°C

5.5.2.2 Propylene Carbonate (30°C)

When the crystal was heated to 30°C, as shown in Figure 5.9 a very similar plot is obtained as that for the samples run at 25°C however it would appear that the 'noise' has reduced somewhat. Again three distinct peaks are to be noted between 0 and 10° 2θ that are reproduced in the fingerprint region. From these peaks it was possible to calculate an average basal spacing of 43.60 Å. Table 5.4 shows the calculation of basal spacings for the individual clay samples and the overall mean. The overall mean of basal spacing was found to be 44.13 Å with a standard deviation of 0.63.

5.5.2.3 Propylene Carbonate (40°C)

Figure 5.10 shows the XRD plot for the clay run at 40°C, the peaks are much sharper than the peaks obtained at lower temperatures and the characteristic peaks as seen earlier are noted once again. Note that the peaks in the mid range 2θ (14 – 20° 2θ) are also more clear. It would appear from the XRD plots that a combination of increasing the experimental temperature and the addition of propylene carbonate has an effect on sharpening the peaks and this may be on account of greater ordering in the crystal. The summary table (Table 5.5) shows that the overall mean of the basal spacing was calculated to be 43.43 Å with a standard deviation of 0.99. This is slightly lower than the mean calculated for the samples run at 30°C. This cannot be deemed as truly significant since at these temperatures, the quaternary ammonium compound is in a state of phase transition and it is not possible to account for what quantity of each hydrocarbon chain length is present at the surface. In addition, these slight increases in basal spacings could imply that some propylene carbonate molecules were able to penetrate the layers where they would preferentially migrate to the surface of the clay. This could cause weakening of attractive forces and possibly initiate steric hindrance of the quaternary ammonium compound on the surface.

5.5.2.4 Propylene Carbonate (50°C)

Figure 5.11 shows a representative XRD plot for a sample run at 50°C. Firstly it should be noted the importance of good alignment of the crystal by the dramatic effect it has on the intensity values. Four clear, sharp peaks are represented in the 0-10° 2θ region of the plot. These are clearly reproduced in the fingerprint region between 24-32° 2θ region. Consistent equidistant peaks for the samples run at 50°C enabled confidence in basal spacing calculations giving an average of 47.70 Angstroms. Table 5.6 shows the summary of the basal spacing calculations and the overall mean of 46.71 Å with a standard deviation of 1.86. Comparing these results with the results of the samples run at 25°C it is clear that there has been a significant effect in the swelling between the layers of the clay. The clay has swelled by approximately 13% in the presence of propylene carbonate at a temperature of 50°C. This would indicate the importance temperature has in the mechanism of swelling clays. It would appear that the effect of temperature is twofold. Firstly, the phase transition that the quaternary ammonium chloride compound undergoes at 50°C has a slight effect on basal spacing as the results from the dry clay show. Secondly, at temperatures where this phase transition has occurred aids the intercalation of propylene carbonate between the crystal layers. The affinity that propylene carbonate has for the surface of the clay clearly enhances the degree of swelling between layers.

5.5.2.5 Propylene Carbonate (50°C Sample Repeated at 25°C)

Due to time limitations on the equipment, it was only possible to run one sample of the organically modified clay that had been treated with propylene carbonate and heated to 50°C and then allowed to cool back to 25°C and scanned again. It is however worth mentioning the results obtained since it indicates the importance temperature has on basal swelling. Figure 5.11 shows the XRD plot for this sample. The average basal spacing that was calculated for this sample was found to be 42.09 Å that is over 4 Å lower than when the crystal was scanned at 50°C. At 25°C, the quaternary ammonium would have cooled back to its semi-solid phase and therefore the hydrocarbon chains would be more ordered and it would seem that the attractive forces between layers would have increased. Although conclusive remarks may not be based on a single experiment, it is possible to say that this does indicate the importance temperature has on the swelling of clays and that even in the presence of a polar solvent, the swelling is not a permanent effect. And basal spacings will revert back to original *d* spacings at lower temperatures.

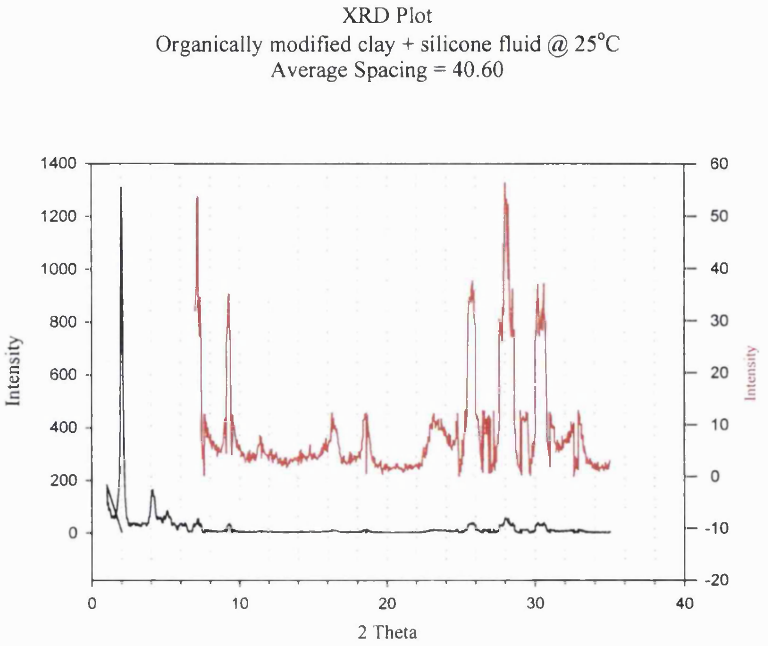


Figure 5.12 XRD Plot of clay and silicone fluid scanned at 25°C

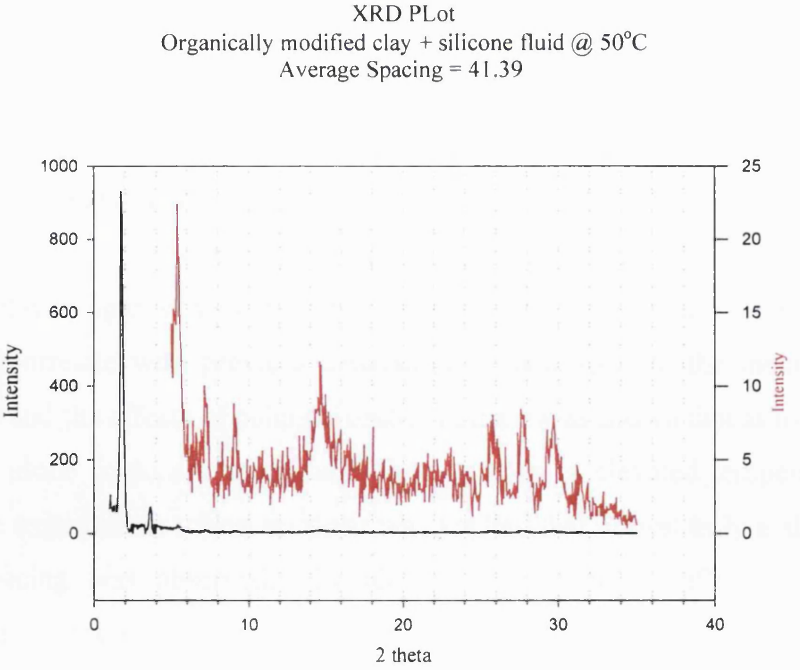


Figure 5.13 : XRD Plot of clay and silicone fluid scanned at 50°C

5.5.3 Organically Modified Eucatex Clay and Silicone Fluid

Figures 5.12 and 5.13 show the results of the XRD plots of organically modified Eucatex clay and Silicone Fluid at 25°C and 50°C. From the results in Chapter Three that detail the effect of polar and non-polar solvents, an increase in basal spacing would not be expected for the samples run with silicone fluid. The results in the XRD plots confirm that no swelling of clay is observed. There is little difference when the sample is heated to 50°C with average swelling increasing less than one Angstrom from 40.60 Å to 41.39 Å. It should be noted that attempts for reproducible results to be made with samples run with silicone fluid were made however the definition of distinct peaks was not clear on any of the plots. This could be accounted for by the fact that the quaternary ammonium chloride is not compatible with silicone fluid and therefore silicone fluid will not naturally have a preference to intercalate between platelets. In addition, the factors as described earlier for the dry clay samples such as the effects of water or uneven coating of quaternary could account for the reason why broad bands with numerous peaks were observed. Nevertheless, it can be concluded that silicone fluid does not promote swelling even at elevated temperatures.

5.6 Summary

The X-Ray diffraction results obtained from this study have shown that temperature appears to play a significant role in the swelling potential of hydrophobic clay. The results also correlate with previous observations made in both the mechanical shear experiments and the effects of polar solvents. There it was shown that at low shear rates temperature alone could not delaminate platelets even at elevated temperatures which was in these experiments where no shear was applied that at best only a slight increase in basal spacing was observed. In addition, the profound effect that propylene carbonate had on the swelling effect at elevated temperature correlated with prior result that indicated that propylene carbonate had a significant effect on swelling. However, the results here showed that in order for propylene carbonate to have a significant effect on swelling, a secondary force was required, in this case in the form of thermal energy. Here it is worth mentioning that the prior experiments show that mechanical energy (particularly very high shear rates) had the greatest effect on delamination of platelets. However, it should not be overlooked that at such shear rates, the energy expended in the form of heat is extremely high and is likely to be a significant factor in dispersion. Finally, the results from XRD also confirm that propylene carbonate does have a strong affinity to the surface of clays as was first described in the surface force measurements and electrophoretic experiments.

CHAPTER SIX

DISCUSSION

6.1 Introduction

In order to gain an insight into the creation and microstructure of the gel phase that Bentone 38 forms in a non-aqueous fluid, three different aspects of energy that may contribute to gelation were investigated. Primarily, chemical energy in the form of polar activators was studied. Chemical activators are quoted in all references as being essential to form a gel structure and it was therefore necessary to explore the role of polar molecules as described in many of the texts. The interaction of polar activators with Bentone 38 was studied using the process methodology and equipment that is readily available in formulating laboratories and as recommended by the suppliers of Bentone 38. From this study, it was possible to identify the most effective polar activator (propylene carbonate) and this was selected as the standard polar activator for later studies. Bentone 38 is a derivative of montmorillonite clay and therefore has a potential to swell. X-ray diffraction was selected as the technique to investigate swelling characteristics. To gain an insight into the way in which a polar activator interacts with Bentone 38, electrophoretic mobility was studied. Finally surface force measurements were also carried out to determine the ease of separation of platelets.

The second phase of study focused on processing. This is the area that the literature is most vague with regards specific details of processing parameters. While it is acknowledged that shear is required to form an organoclay gel the processing regimes are not defined. A range of equipment were evaluated to determine which was the most effective at delamination of clay particles and if any provided the means to creating a gel network without the aid of polar activators. In conjunction with the evaluation of processing equipment, thermal effects were also investigated. Finally, an explanation to the microstructure of the final product attained was attempted by means of evaluation through electron microscopy.

6.2 Polar Activators

It is without doubt that polar activators interact with Bentone 38 and thereby contribute to the rheological modification of overall product viscosity. All the polar activators investigated increased the bulk viscosity of the Bentone 38 suspensions by differing degrees. These next sections endeavour to explain the results obtained and where appropriate indicate where further investigation would be required.

6.2.1 Swelling Behaviour of Bentone 38

The initial study was to compare the effect of silicone fluid (non-polar) against two polar fluids (ethanol and propylene carbonate). By simply shaking Bentone 38 in a vial with each of the test fluids, it was clear that the polar activators interacted with the clay by the significant increase in swelling ratio by increasing the swelling ratio by 2.5 times that for silicone fluid. It also provided evidence that the non-polar silicone fluid did not have an effect on swelling ratio. When the procedure was repeated for formulations of Bentone 38 and silicone fluid with varying quantities of the polar activators (between 1 and 20%), the results obtained gave significantly better (higher) swelling ratios than that were recorded for the samples prepared using neat polar activator. A further increase in swelling ratio was obtained when the samples prepared with propylene carbonate were sheared using a standard laboratory homogeniser (Silverson L4R 'dip-in').

These experiments were the introduction to Bentone 38 and the non-polar fluid in the presence of polar activators. They were designed to test the claims laid down in the supplier literature (referred to in Chapter One) that polar activators are essential to create a gel network. The experiments confirmed that polar activators do appear to play a role in swelling Bentone 38. They also provided the evidence that a polar activator must be introduced to a formulation as an additive and that a carrier fluid such as non-polar silicone fluid is required to effect better swelling. Finally the experiments also confirmed that shearing the products with a homogeniser had a significant effect on the swelling ratio of Bentone 38. What these experiments did not confirm was that the Silverson homogeniser was suitable for creating a gelled product since all of the samples, regardless of polar activator to clay ratio, were found to be unstable and none of the samples could be described as gels. Although there was a visible increase in product viscosity, each sample was prone to sedimentation. This conflicts with the trade literature (Rheox Ltd) that quotes such a homogeniser as a suitable means for creating a stable gel using formulations included in this matrix of experiments.

The following may be said:

- It is assumed that since it was not possible to manufacture a stable Bentone 38 gel using the guidelines dictated by the supplier literature, an effective dispersion of agglomerates had not been achieved even in the presence of polar activator. Consequently, it can also be assumed that the literature that refers to dispersed particles must be considered with caution since it is unlikely that a true dispersion was achieved during these experiments.
- Polar activator clearly plays a role in increasing product viscosity and it would appear that the polar activator intercalates between the platelets and causes a certain degree of platelet swelling but it cannot delaminate clay platelets in its own right.
- The polar activator also needs to be present in a diluted form since neat polar activator did not swell the clay as efficiently as when silicone fluid was present as a carrier. The silicone fluid did not appear to contribute to clay swelling.
- The shear exerted by the Silverson homogeniser was not sufficient to delaminate the clay agglomerates to form a structured gel even with the polar activator present. This may be due to a number of factors. Firstly the shear rate of the Silverson homogeniser may not be sufficiently high enough to delaminate agglomerates of Bentone 38 clay to the primary particles and that when agglomerates were of a certain dimension they would pass through the homogeniser without further delamination. Secondly, the amount of time the mixture was subjected to the shear device may not have been sufficient. Thirdly, the design of the 'dip-in' Silverson is

such that not all of the mixture may have been subjected to the same quantity of shear.

It was these first experiments that directed the design of subsequent studies to investigate the effectiveness and role of polar activators and more significantly, the importance of process methodology to creating a gel network.

6.2.2 Sedimentation of Bentone 38

The sedimentation studies investigated the effect of different polar activators. These were selected based on the rating of efficacy as a polar activator quoted in appendix 2.1, their functional group and those recommended by the trade literature.

The process methodology used for this series of experiments was designed to ensure that the entire product had been subjected to the same degree of shear through a Silverson homogeniser. The homogeniser was also selected since it is recommended by the suppliers of Bentone 38 as suitable for effectively dispersing the clay platelets in conjunction with polar activators. An in-line Silverson homogeniser was used for these experiments and each product was subjected to five complete shear passes. This ensured that the time duration for shearing exceeded the duration that had been recommended by the suppliers (>10 minutes). Temperature was controlled to minimise any thermal effects that could contribute to delamination of clay platelets. It is only possible to minimise thermal effects to a certain degree since the work performed at the shear head always creates a thermal gradient and it is not possible to separate these two effects completely. To minimise the thermal effects, cold water was run through the delivery and receiving vessels to keep the product at a temperature below 20°C.

The results from these experiments showed that once again, regardless of the polar activator used, a gel network was not created; however each polar activator had an effect on increasing the product viscosity. Each formulation investigated was unstable and prone to significant syneresis. The most efficacious polar activator was propylene carbonate while the least was propanol. There was a trend that the lower chain alcohols (methanol and ethanol) were almost identical in sedimentation rate as were the ketones (propanone and acetophenone) that yielded a slightly lower end sedimentation level. Nitroethane was effectively equivalent to the lower chain alcohols. The control (no polar activator) and the non-polar additive (hexane) sedimented immediately and displayed no increase in product viscosity. Viscosity measurements and rheological measurements correlated these results.

The following points can be considered:

- It is not clear why propanol gave consistently poor results for structuring. This contradicts the observations of Gheradi and colleagues (Gheradi et al, 1996) who found that the alkyl chain length of alcohols (C_1 to C_8) in the sol-gel transition for trioctahedral clays in non-aqueous fluid resulted in exactly identical sol-gel transitions. There is no detail of the clay used although it is referred to as organo-bentone and it can only be presumed that the clay is of a similar nature to Bentone 38.

- The reason for propanol being less favourable than the other polar activators is not a factor of molecular dimension or dipole moment since it lies in the middle of the range of the other polar activators investigated. One possible explanation is the isomer selected for this assay. The propanol selected was the iso-propyl alcohol (propan-2-ol) isomer. It is possible that the position of the OH functional group is important and therefore the isomer propan-1-ol may have better structuring qualities.

- There was also no correlation of functional group and structuring efficacy since propylene carbonate, propanone and acetophenone all possess carbonyl groups yet did not rank equivalently. An investigation into the optimum polar activator was out of the scope of this study. This would require a vast survey of polar compounds based on their functional group and including their chemical analogues. As such only a very limited number of potential polar activators were being investigated to determine whether there were significant differences between polar activators. It can be concluded that this is true and that the three polar activators that are recommended by the manufacturers of Bentone 38 (propylene carbonate, methanol and ethanol) are the most efficient. The manufacturer also suggests that propanone is also an effective polar activator however our studies showed that it is less efficacious.

- Solubility of the quaternary ammonium group in the polar activator could be one factor that would account for differences noted between those tested. Alternatively, polar activators may be attracted to the surface of the clay and either preferentially exchange with the quaternary compound or cause the quaternary compound to reposition via steric hindrance that would account for the swelling observed. An experiment to determine whether the quaternary ammonium was preferentially replaced or solubilised by polar activator would be to measure the quaternary ammonium content in the liquid phase before and after the addition of polar activator.

The optical microscopy images clearly indicated that complete dispersion of agglomerates to primary particles had not been achieved for any of the series using the process methodology described and the range of polar activators. The micrographs also did not provide evidence of a network microstructure between the agglomerates since the agglomerates appeared to be discrete entities. There was evidence that there was a greater range of agglomerate particle sizes with the samples that contained polar activators than the control samples. This indicated that shear had an effect on particle size by partially reducing agglomerates. The presence of a significant number of large agglomerates in all the samples provided evidence that the use of a homogeniser did not sufficiently delaminate clay platelets and explained why a gel network was not created.

The results showed that polar activators in combination with shear through a Silverson in-line homogeniser contributed to increasing product viscosity but a gel network was not created. One possible explanation for this would be that the polar activator diffuses to the surfaces of the clay. Through intercalation of polar activator between the platelets swelling occurs. It is possible that the degree of swelling would depend upon the efficacy of polar activator. The swollen agglomerates are disrupted as they pass through the homogeniser head and broken down to smaller agglomerates however a gel network is not observed because not enough primary particles or small agglomerates are created to form a structure that is stable. Instead the increase in viscosity recorded could be a result of the increased number of particles having smaller dimensions that would occupy a greater volume i.e. would be space filling. The fact that only weak attractive forces may exist between agglomerates means that the force of gravity will overcome these over time and the larger agglomerates will be seen to sediment rapidly. The samples with the greatest number of large agglomerates, i.e. the samples where polar activator had been less efficient at swelling the clay would be noted to sediment first.

The sample with the non-polar hexane and the control sample sedimented rapidly and yielded very low viscosity measurements. This confirms that polar activator is required in the formulation to aid the breakdown of platelets. This study corroborates the principle of the mechanism for dispersion as quoted by Rheox in that polar activators encourage swelling of agglomerates and the action of shear breaks the particles down in size. However, it may be concluded that a complete dispersion of platelets was not achievable with this mechanism and therefore a gelled product was not created.

From the micrographs of the suspensions the agglomerates appear to be more spherical or ellipsoidal in shape rather than the sheet or plate-like description of a dispersed organoclay. These agglomerates of unequal sizes and densities will settle at different velocities. Sedimentation is a complex area and consequently the details of the processes that convert suspensions to sediments are still not fully understood. There are numerous factors that effect the rate of settling. This includes the hydrodynamic effect of neighbouring particles that may increase or decrease the sedimentation velocity of a particle. Repulsive forces also hinder settling whereas attractive forces induce aggregation causing particles to settle as an effectively larger entity and thereby increase the velocity. In both cases the net effect reflects the spatial distribution of particles, or the microstructure of the suspension. Other factors include Brownian motion, gravitational forces and interparticle potential. No attempt has been made to try and equate the rates of settling of sediment in this study. However, there are a number of points to be considered that are:

- The effect of polar activator and shear gives an overall reduction of particle size and therefore sedimentation of these suspensions would be expected to take longer than the samples that had no polar activator if gravitational forces were only being considered.
- The fact that the polar activator interacted with the clay means that there is likely to be an electrostatic effect that would influence the attractive and repulsive forces between the agglomerates and therefore have an effect on stability of the sediment.
- The control samples sedimented immediately indicating that the polar molecules influence stability of the clay.

6.2.3 Interactions of Polar Activators with Organoclays

Surface Force Measurements (SFM), Electrophoresis and X-ray diffraction were applied to investigate and to develop further understandings of the way in which polar activators react with clays.

The model clay Mica was used for the SFM experiments for two reasons. Firstly, the dimensions of Bentone 38 are below the capabilities of the experimental equipment whereas mica is available as large sheets. Secondly, mica is considered to be molecularly smooth when sheets are cleaved apart. It is a requirement of the SFM technique that surfaces are molecularly smooth to produce resolution down to 10^{-10}m resolution. Since the chemical structure of mica and montmorillonite are both planar dioctahedral species, mica was assumed to be a representative model for montmorillonite. Efforts were made to coat the mica with the quaternary group (Arquad 2HT) however a satisfactory monolayer coating was not achievable. Consequently the results obtained measured the interactions of the additive (propylene carbonate) and the bare clay-like mica surfaces in a non-aqueous environment.

To recap, SFM data can only enable a description of the forces between interface pairs and therefore extrapolation to platelet stacks and agglomerates that exist in reality may only be made tentatively. Additionally, the nature of the SFM techniques only allows measurement of the forces that exist between the faces of clay crystals therefore the edge effects that are attributed to play an important role in the development of the gel microstructure cannot be considered. (van Olphen, 1991).

The results of the SFM experiments displayed a number of points. After the mica sheets were separated and then the distance between separation was reduced, no double layer repulsive forces were recorded. This correlates studies performed by Christenson and Horn (1985) where even at separations as low as 9nm, the long-range repulsive force was recorded to be zero for octamethylcyclotetrasiloxane (D4 cyclomethicone) and mica. When polar activator was added to the silicone fluid there appeared to be some short–range repulsion as the mica sheets were brought into contact. However, long range repulsive forces were not measured. Christenson and Horn also showed that long-range repulsive forces were only apparent when the addition of electrolyte was introduced and this was attributed to the development of an electric double-layer being created. For systems where double layer repulsion was low as for our systems, the attractive van der Waals forces took precedence.

It was also not possible for the sheets to return to zero separation (i.e. mica-mica contact) which implies there was a barrier present. This also correlates with the work performed by Christenson and Horn (1985). Solvation forces are normally observed as oscillations, however the data recorded did not display this. This has been attributed to a smoothing effect (Christenson, 1985) noted in systems that contain water or are composed of different sized molecules. The lack of oscillations in the recorded data could be a result of either of these factors since the silicone fluid used was a blend of cyclomethicones (D4 and D5) and was also unlikely to be completely free of water molecules despite attempts to dry the fluid.

The most significant results were for adhesion force measurements. In particular, the system measuring the solvent saturated with water (24hrs) increased the adhesive energy between mica surfaces by as much as three times compared to the unsaturated silicone fluid samples. The samples that had been saturated with propylene carbonate also displayed strong adhesive forces. Adhesive forces were noted to be reduced slightly by oscillating the mica sheets with an amplitude of 1000 Hz over a few hundred microns. This provided evidence that polar activators are strongly attracted to the surfaces of clay.

Considering the above, the results that were obtained enables an insight into the way immiscible polar activators may interact with the clay surfaces of Bentone 38 and how they may contribute towards building a gel microstructure. From the work that was performed looking at dispersion and swelling, the data suggests that there is a clear and important role for activators in modifying the rheological properties of Bentone 38. X-ray diffraction studies have shown that the immiscible polar activator intercalates between the stacked platelets and interacts at the surface of clays effecting a degree of swelling. This is particularly important at elevated temperatures. There is also evidence from the sedimentation work that there is a ranking order of efficacy of polar activators in silicone fluids with propylene carbonate being the most powerful solvent. Silicone fluid that does not appear to intercalate the platelet stacks or cause swelling is likely to be a poor solvent. Despite no repulsive forces being measured for uncoated mica crystals, it is probable that repulsive forces would exist if surfactant quaternary ammonium compounds were present as with Bentone 38. Therefore, one possible explanation for the swelling observed in the Bentone 38 systems and where vermiculite was coated with surfactant (XRD studies) would be that the polar activator may produce large, short-range repulsive forces as a result of the hydrophobic surfactant group being forced to re-orientate on the surface.

Conversely the attractive forces also need to be considered. From the work done on electrophoretic mobility it is known that polar activator concentrates at the surface of Bentone 38 effecting the electronic charge of the particles. It is possible that the polar activator penetrates between the quaternary groups to form an immiscible layer around each particle. The SFM adhesive studies showed that both propylene carbonate and water were observed to have no long-range effects on repulsion between the mica sheets but they had a significant effect on the adhesive forces. It is possible that the polar activator condenses on the surface of the clay and causes a capillary mechanism that leads to an apparent attractive force at a distance that pulls the surfaces in adhesive contact from up to 0.1 μm providing a route to agglomeration of clay particles.

The reason why Bentone 38 is not observed to be optimally dispersed to primary particles when processed through a Silverson homogeniser may be a consequence of these two forces counteracting with each other. If the polar activator diffuses to the surface of the clay and causes the quaternary compound to be disrupted, repulsive forces between the surfactant molecules would force the platelets to swell. At the same time, attractive forces work to pull the platelets together. At a certain point, an equilibrium would exist whereby platelets appear to be swollen but the shear rate of the Silverson is not sufficiently high enough to disrupt the attractive forces below a certain size. In addition to this once the shearing action has stopped, some agglomerates may preferentially reagglomerate depending on whether they are in close enough proximity to an adjacent particle for the short-range forces of attraction to come into force. With the onset of sedimentation, as the larger particles fall to the bottom of the vessel, particle-particle interactions would increase and as a result flocculation of particles would become more apparent.

From the previous swelling studies it was shown that polar activator alone is a poor dispersion medium and that silicone fluid is required to optimise swelling behaviour. If a completely anhydrous organoclay gel is considered and consider only the face to face interactions between the platelets, the adhesion between the dry organoclay surfaces will determine the strength of the bonds between the gel. If polar activator is then introduced and allowed to equilibrate throughout the gel, the adhesive contacts will increase in strength as the clay surfaces become coated by propylene carbonate rather than silicone fluid. If the edges also have an attractive effect, the combination between the forces and random ordering of platelets throughout the sample would enable the theory that a greater gel strength would exist. If the propylene carbonate condenses on the surface of the clay adhesive forces appear to pull the surfaces into contact. The platelets may then begin to reagglomerate reducing the concentration of dispersed clay particles for structure formation. This would result in gel strength being reduced and hence the importance of the level of polar activator in a formulation.

The structure of the organoclay gel is clearly dependent upon adhesive contact and therefore the concentration of polar activator, overall number of contacts and uniformity of activator distribution are likely to be critical. These latter two factors are heavily dependent on the processing method used for dispersion. In other words, the effect of polar activator on swelling Bentone 38 is insignificant without a means of delaminating the platelets since the attractive forces between platelets prevent them completely separating. The attractive forces will preferentially cause agglomeration and consequently a very weak and unstable gel will be formed. The forces of attraction between the agglomerated particles are lower than the strong adhesive forces between individual platelets (Christenson, 1985) and can rearrange during settling and gradually compact into a high phase volume sediment as observed in the previous sedimentation studies.

The role of the quaternary ammonium group must also be considered. Producing a wetted clay surface and providing a diffusion path for activators to intercalate between the platelet layers is critical to dispersing the clay. Once the clay has been dispersed, the role of the quaternary ammonium on the surface of the clay is likely to be restricted to preventing re-establishment of the electrostatic bonds between bare clay surfaces by short-range steric hindrance.

Having considered the repulsive and attractive forces of mica clay as a consequence of the addition of polar activator, it was necessary to establish the effects of addition of polar activator with Bentone 38. This was carried out using electrophoretic mobility studies. This included firstly identifying whether Bentone 38 is charged at all in the presence of silicone fluid and then to determine whether there was an effect of charge sign and magnitude with the addition of a range of polar activators.

The electrophoretic studies were performed using dilute suspensions of Bentone 38 clay gel particles to firstly determine the net charge and to examine the effect of various polar activators on the charge sign and magnitude. A dispersion of Bentone 38 clay and silicone fluid was prepared and polar activators were dosed into the environment to determine the changes on electrophoretic mobility

One of the important points to note regarding the results obtained is that firstly, particles in the untreated silicone fluid showed no effect on electorphoretic mobility. When polar activators were tested, no region was identified in which electrophoretic mobility was invariant with respect to the field strength. There are a number of possibilities why these fluctuations were observed.

- The particles may be polarisable that would account for the almost linear relationship between field strength and mobility for particles dispersed in silicone fluid activated with propylene carbonate and samples activated with carbonyl containing molecules.
- There may be flocculation formation as a consequence of adding polar molecules to the system. This may be a factor of the methodology of sample preparation for ELS in that : since these experiments applies a very high strength uniform electrical field and based on the knowledge from SFM, in the presence of polar activator strong adhesive forces exist between clay platelets that are partially dispersed, it is possible that by diluting the test gel and disrupting its network during mixing the particles could be forced to collide and build up flocs or agglomerates by overwhelming adhesive forces. On standing, flocs or agglomerates could continue to grow. Then, when the field was applied a combination of the electrostatics and shear through shaking the sample prior to the test may cause the agglomerate to break down again. As such the whole mixture could be dynamic and therefore account for the variations with field strength.
- Another factor could be that the particles are forced to reorientate or distort in strong fields when the particles are accelerated to high velocities. Values for particle drag coefficients for at low Reynolds numbers show that all particle orientations are stable in free fall that implies that a randomly orientated particle population will display a range of velocities dependent on their original orientations. The influence of field strength upon orientation then becomes highly complex since it is reported

that the drag factor for flat disks may be five times that for spheres of similar radius (Perry, 1981).

Despite the above factors the trends in the mobility data were repeatable and consistent. Propanone and Propylene Carbonate showed that particles became negatively charged. Ethanol and Cyclohexane produced a slight positive shift. The hexane derivatives all produced positive shifts whereas methyl ethyl ketone and methanol produced largely negative shifts.

One explanation for why negative shifts are produced by some activators could be that they may effectively solvate the dimethyl dialkyl quaternary ammonium ion in the silicone fluid environment. The solvated cation could then be transported into the bulk silicone fluid leaving the clay surface with its underlying negative face charge. Alternatively, accumulation of activator at the organoclay surface would allow local ionisation and therefore a high surface conductance making the particles highly polarisable and electrokinetically active.

Where the charging appears to be positive (no additive, ethanol and hexane derivatives) implies that mobility is unchanged by these additives with variations being caused by experimental factors alone. The mechanism for a real positive charging is not clear. It could be simply be because Bentone 38 may be covered with an excess of cationic with respect to the available sites for isomorphic substitution. This would require the presence of balancing anions. Ionisation of these anions from excess surfactant located at the surface would render the particles more positive.

Linked to this hypothesis, the role of clay platelet edge charges that are positive must also be balanced with counter-ions. Removal of these counter-ions would cause the edges to be positive and thus the entire clay would have a net positive charge.

The fact that particle charging exists in a non-aqueous medium has a number of implications. Charging requires ionisation of the surface in question and, since the only labile ions available originate from the organoclay in question are the cationic quaternary ammonium groups, it is these that are likely to become solvated. It is possible that the cations are removed from the surface to form a diffuse double layer that would induce greater repulsive forces and account for the swelling behaviour noted in the presence of polar activator. Alternatively, polar activators being strongly attracted to the surface of organoclays, could concentrate at the clay surface in a compact monolayer.

In aqueous systems, charging appears to play a significant role for providing bonds to create a network microstructure by building face to edge, edge to edge and face to face linkages. This is due to the existence of an electrical double layer and plays a leading role in colloidal stability. The electrical double layer in non-aqueous environments is often non existent mainly due to the significantly lower level of ionisation achievable. Furthermore, the long range of the electrical force in non-aqueous media due to low dielectric constant and low ionic shielding causes aggregation to lessen the energetically unfavourable double layer overlap. In a fully dispersed Bentone 38 gel, where there would be a high concentration of individual particles forced to be in contact could result in the effect that any double layer repulsion would be greatly overwhelmed by short range attractive forces such as van der Waals forces. In addition to this, the presence of the polar activator, concentrated at the surfaces of the clays may also induce interparticle bonding such as hydrogen bonding.

From the SFM work, evidence was shown that the presence of water had a significant effect on intersurface adhesion. In the electrophoretic studies, it was shown that water did not enhance the generation of negative charges on individual clay platelets. This provides evidence that while propylene carbonate (which generates a negative charge) is an effective swelling agent, it does not give as good adhesive properties as water. Conversely, water causes immediate flocculation when added to the system indicating that it is a poor swelling agent. Additionally, ethanol and methanol had opposite effects on particle charging yet gave similar results on swelling of platelets in the sedimentation studies. It is therefore feasible to assume that the charging of particles as a consequence of polar activator is not a key factor as to the effectiveness of swelling. The results imply that some activators are good swelling agents but are not necessarily good gelling agents. The trade literature advises the addition of a small amount of water to the formulation and it is clear now, that the role of water is to enhance the stability of the gel formed as a result of the strong interparticle attractive forces.

Propylene Carbonate has been shown to be the most effective polar activator in the absence of water other than what is found as trace amounts. Propylene carbonate is immiscible with silicone fluid and has a strong affinity for the surface of organoclays. By capillary condensation and destabilising the surface of the organic layer on the clay, it is possible that propylene carbonate would form solvating layers at the surface of the clay that causes swelling to be observed. Since propylene carbonate has a strong affinity for the surface of the organoclay, it is possible that when the level of polar activator is increased, a concentrated immiscible polar layer would form between the platelets. This would account for why above a certain concentration, the polar activator is actually observed to act as a degellant rather than as a gelling agent. This would explain the poor swelling behaviour observed when clay was completely saturated in propylene carbonate.

The final study of investigating the effect of polar activators had on swelling clays was a study using X-ray diffraction. Once again a model clay was used. This time vermiculite clay coated with Arquad 2HT (dimethyl dioctadecyl ammonium chloride).

The results showed that at 25°C, no significant effect on swelling occurred, even in the presence of polar activator. However, when the XRD was run at elevated temperature (50°C), there was a significant increase in basal spacing. The most notable increase was with propylene carbonate however a slight increase was noted in the absence of any solvent and in the presence of silicone fluid at elevated temperature.

There are a number of points to note. Firstly, it is possible, that at 25°C, propylene carbonate could not intercalate the platelets effectively on account that the clay crystal could not be immersed in the test solvent and relied upon a saturated environment. It is presumed that dosing the crystal several times with a pipette full of test solvent and maintaining a saturated environment should have ensured sufficient polar activator to contact the clay. This suggests that intercalation does not occur through adsorption alone and that a secondary requirement is needed. As the temperature was increased to 50°C, there was a significant increase in basal swelling. XRD measured a maximum increase of 6-7 Å when propylene carbonate was added to the system. This raised the question that thermal energy may contribute to aiding the swelling capabilities of clays. From work investigating the effect of temperature on Bentone 38 (which will be discussed later) a clear phase transition occurs with the quaternary ammonium compound on the surface of the clay. Elevated temperature alone had a slight effect on increasing the basal spacing of clay however, the truly significant increase was only noted when polar activator was also present.

It is possible that the steric arrangement of the quaternary ammonium is effected by the addition of polar activator. It is known from electrophoretic studies that the charge on the clay is altered and from SFM studies that propylene carbonate has a strong affinity for the surface of clay. This could cause the quaternary ammonium to realign and have a swelling effect. In addition, based on work reported in the text by Grim (Grim, 1968), at concentrated levels, quaternary ammonium compounds lie almost perpendicular to the surface of the clay with the hydrocarbon portions of the organic in the energetically more favourable trans, trans configuration forming however, with the addition of polar molecules a degree of unravelling of the hydrocarbon chain may occur. As further evidence that the effect of swelling is most likely to be attributed to steric factors rather than solvation through the polar activator is seen when the samples were allowed to return to 25°C and the original basal spacing dimensions were again recorded. This would indicate that swelling is not brought about through an exchange of quaternary with the polar activator.

The XRD studies gave evidence that the effect of temperature on the swelling behaviour of clay was significant. Surprisingly, this is an area that has never been associated with the properties or efficacy to delaminating clay platelets or that it may contribute to the structuring mechanism of the gel network of organoclays.

From this work, it was decided that a greater focus into the mechanism of delamination of particles from a mechanical and thermal perspective would be considered.

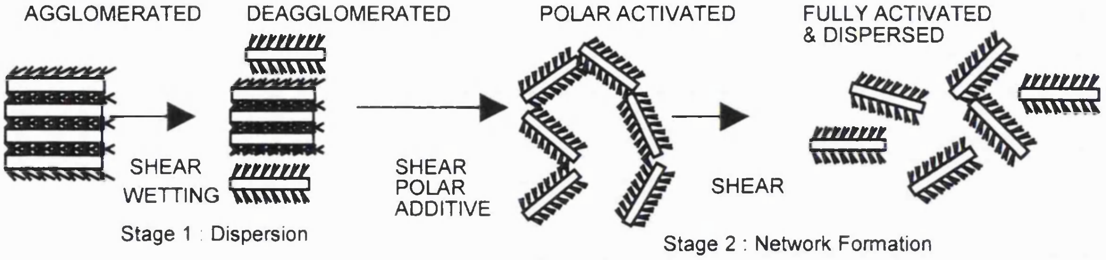
6.3 Dispersion through Processing

The term 'dispersion' is quoted widely in open literature with respect to Bentone 38. Dispersion can have different meanings although in the case of this study it means the complete process of incorporating powder into a liquid medium such that the final product consists of fine particles distributed throughout the medium. The process of dispersion is an area that much time and effort has been devoted to by chemical engineers. In the context of Bentone 38, it is apparent that little focus has been invested in the actual process mechanism and that attention has featured entirely on the 'key' ingredient, the polar activator. There follows an attempt to highlight the importance of choosing the correct processing equipment and methodology in order to delaminate the organoclay particles and thus create the described gel microstructure.

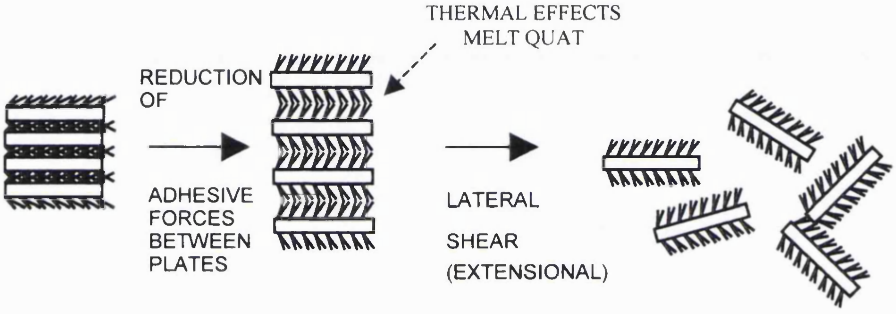
Bentone 38 consists of aggregates of small particles. The hypothesis proposed in this study was that polar activator was not critical to creating an optimum dispersion and network but that mechanical energy alone or in conjunction with thermal energy could delaminate platelets and build a homogenous dispersion. The second part of this hypothesis is that the role of the polar activator (if required) is not primarily to swell the platelets and aid dispersion but rather to prevent flocculation of freely moving particles. The role of the polar activator would be to associate with the clay surfaces to create reactive interfaces on the particles to enhance a gelled microstructure. The two mechanisms are shown schematically in Figure 6.1.

Scheme (a) shows the mechanism that is currently published as the way to create an optimum gel network. (Rheox Ltd)

Scheme (b) shows the alternative proposed mechanism as a consequence of the studies performed.



Scheme (a) = Current accepted mechanism



Scheme (b) = Proposed alternative mechanism

Figure 6.1 : The two proposed mechanisms that contribute to network formation

To understand what is required of dispersion the following section details what is commonly accepted as a dispersion process. There are four main stages in a dispersion process :

- Incorporation
- Wetting
- Breakdown of agglomerates
- Interaction of dispersed particles (e.g. flocculation)

A wide range of processing equipment can be used for general dispersion of powders in a blending operation. For powders where dispersion to primary particles is critical, as with Bentone 38, our studies have shown that the choice of mixer and associated process is fundamental for effective dispersion. During milling each of the four processes occurs in some part of the liquid phase. The final result on dispersion depends on a variety of factors such as shear rate, surface tension, viscosity, cohesiveness of the powder as well as the various interactions that occur between the solid surface and the molecules in the liquid phase. Based upon this, it is clear that the Bentone 38 formulation under investigation fit a number of these criteria. It also displays that the concept of dispersion is a complex process and not attributed to one particular element.

When Bentone 38 is added to the surface of the silicone fluid, the silicone fluid begins to penetrate the under surface of the powder and small agglomerates will be engulfed by the advancing interface and become detached from the bulk. Larger agglomerates also tend to be engulfed. Silicone fluid may also begin to penetrate the agglomerate as a slower rate than the engulfing process although there is no evidence of swelling occurring. If polar activator has been added, it is at this stage that it will begin to diffuse and intercalate the platelets of the agglomerates. From electrophoretic, SFM and XRD work there is evidence to show that the polar activator preferentially seeks the surfaces of the clay. This is the wetting stage of the dispersion process. Since Bentone 38 is hydrophobic the silicone fluid is a compatible medium that serves as a wetting agent where primarily the outer surfaces of the particles are wet out. Our studies have shown that silicone fluid does not appear however to preferentially diffuse between the interlayers of the clay agglomerates and that a further mechanism is required to ensure intrinsic mixing of all platelets. The characteristics of the wetting process are dependent on the properties of the liquid phase, the character of the surface, the dimensions of the interstices in the agglomerate and the nature of the mechanical process used to bring together the components of the system. The air trapped between the agglomerates will escape as bubbles as outer particles detach until all the agglomerates are wetted. Note that air can be trapped in systems (aeration) however, this is a factor of viscosity of bulk phase and as a result of the formulation being composed of high levels of powder. The formulations for the organoclay gels have a low level powder content and low viscosity silicone fluid that does not cause aeration to be a processing issue.

When the Bentone 38 has been wetted, the next stage is to break down the agglomerates by a mechanical force. It is generally accepted that breakdown of agglomerates is brought about by shearing and/or impact. Disruption by shearing relies on viscous drag whereas the impact process occurs more easily when unhindered by viscous resistance. The two mechanisms operate under opposing conditions and each process equipment works best within fairly close viscosity limits. The addition of the surface active polar material can be important to both stages both at the wetting stage where swelling of agglomerates occurs but also it may have a stabilising effect of the end dispersion.

The final stage of dispersion is to be able to maintain the particle distribution and prevent flocculation. Flocculation is the process that reduces the number of particles due to collisions between particles, both under Brownian motion and dynamic conditions.

There are three types of interaction that are involved in the approach of particles :

1. The London-van der Waals forces of attraction
2. The Coulombic force (repulsive or attractive) associated with charged particles
3. The repulsive force arising from interaction between adsorbed layers on the particle surface.

These factors contribute to the description of microstructure that is observed following the process of dispersion. In practical terms these four stages of dispersion happen concurrently and are not normally separated out.

The literature, as already stated, does not specify a particular shear regime to be capable of effectively dispersing and gelling clay suspensions but claims that any dispersion homogeniser would be suitable. The evidence shown in this report clearly contradicts this broad recommendation and in fact only the homogenisers that provide extreme levels of homogenisation are capable of delaminating particles. The reasons why a broad list of equipment is posed as being suitable is probably due to the fact that the organoclay is a commercial product and therefore the manufacturers have historically recommended generic equipment.

The local flow in the vicinity of a particle is either turbulent or laminar. In laminar flow, the flow type may be simple shear or it may contain extensional or extensional flow components. For turbulent conditions, another division may be made. If the particle or droplet is smaller than the length of scale of the smallest eddies in the flow (known as the Kolmogorov length) binary break up occurs. If however, the particle is larger than the Kolmogorov length, inertial break-up will take place which is where inertial forces dominate over viscous forces.

The different processing equipment pieces evaluated in the studies for dispersion were selected to span the range of shear rates that are practical within a laboratory or small scale pilot plant. These ranged from an impeller to a very high-pressure homogeniser.

The first equipment to be investigated was a standard laboratory impeller mixer. The advantage of an impeller mixer is that the agitator provides very intense local mixing. This type of mixer is particularly effective for droplet breakdown and dispersion of droplets occurs in regions where high fluid forces are generated i.e. close to the agitator blade. When a droplet experiences high fluid force it will deform and if the force is applied for sufficient time and is greater than the interfacial force, the droplet will break up. The results of the initial experiment of Bentone 38 systems clearly show that the turbulent forces exerted at agitator are not sufficient to delaminate the clay platelets. This experiment was included to show proof of principle that high shear is required for deagglomeration of Bentone 38.

The second type of process equipment to be evaluated was the homogeniser. Two models of homogeniser were investigated, a laboratory standard rotor-stator homogenisers and a pilot scale (30 Kg) double screen in-line homogeniser. For each of the models, the shear rate was calculated by measuring the tip speed and the gap between the rotor and stator. The shear rate is calculated using Equation 6.1.

$$\dot{\gamma} = \frac{n\pi d}{h}$$ **Equation 6.1**

Where n is the rotational speed, d is the rotor diameter and h is the gap width.

The shear rate for the single screen laboratory homogeniser was calculated to be 60,000s^{-1} and for the double screen pilot scale homogeniser 41,000s^{-1}at maximum speed. The difference between these shear rates is not classed as significant however it should be noted that the double screen homogeniser increases the residence time particles experience shear since the particle experiences two stages of shear passes. The flow type in a Silverson homogeniser is shown in Figure 6.2. When a suspension enters the gap, the flow will be partially extensional. Inside the gap, the flow is characterised by simple shear flow due to the rotation of the rotor and also axial extensional flow. When the fluid leaves the gap, there is decelerating flow. The dominant flow is accepted as rotational shear.

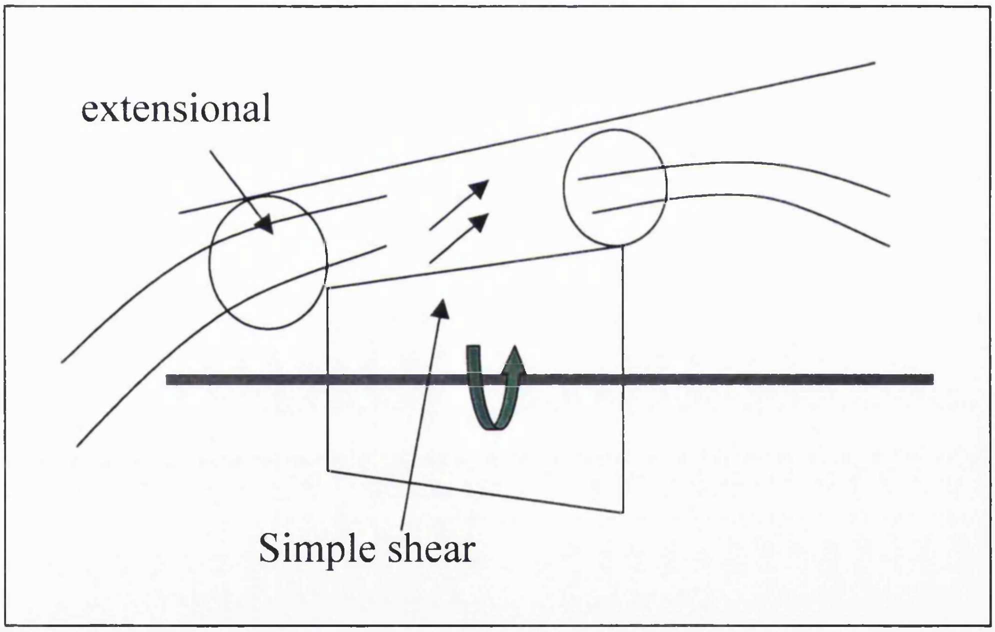


Figure 6.2 : Geometry and flow types of a rotor/stator mixer

To calculate the flow through the in-line dynamic mixers it is necessary to calculate the Reynolds number for the system that is being investigated. The Reynolds number is the number that relates the ratio of inertial forces to its drag forces. It has been demonstrated that it is not velocity of fluids but the Reynolds number that is the most important determinant of flow pattern (Baker, 2000). By plotting the Reynolds number against the Power number calculated for the equipment it is possible to determine whether the flow is turbulent, transitional or laminar. The Power number (P_o) is calculated by measuring the power of the motor and substituting into equation 6.2

$$P_o = \frac{P}{\rho N^3 D^5}$$ **Equation 6.2**

Where P is the power draw from the homogeniser motor at a specific speed, ρ = density of liquid, N = rotor speed and D = diameter of rotor.

Equation 6.3 is used to calculate the Reynolds number for the Bentone 38 suspension (assuming a homogenous mixture)

$$\mathrm{Re} = \frac{\rho . s . g}{\mu}$$ **Equation 6.3**

Where Re = Reynolds number; ρ = density of liquid; s = tip speed; g = rotor/stator gap and μ = viscosity.

For a sample of Bentone 38 test suspension with a viscosity of 100 cP the Reynolds number was calculated to be 67.04. At 300 cP the Reynolds number was 22.35. This was calculated from a product density of 1.000 kg/m^3 @20°C Figure 6.4 shows a chart that compares the Power number calculated for a Silverson Double Screen homogeniser to Reynolds number (Baker, 2000) as calculated for the pilot plant scale homogeniser. This graph represents a model of the flow patterns that are capable in a Silverson homogeniser. Distinct regions determine the flow patterns that are controlled by critical Reynolds numbers that have been calculated to be between 50 and 500 Re. The region between the critical Reynolds number for laminar flow and that for turbulent flow is deemed the transitional region. It is unclear whether dominant break-up of matter within this region is the result of laminar or turbulent mechanism or a combination of both.

Calculating the Reynolds number for the Bentone 38 system at 100cP (at the start of homogenisation) the particles were subjected to transitional flow, the region between laminar and turbulent. As shear time was increased the viscosity was found to increase.

Recalculating the Reynolds number and using the model from Figure 6.3, the flow through the homogeniser head was noted to change to laminar flow.

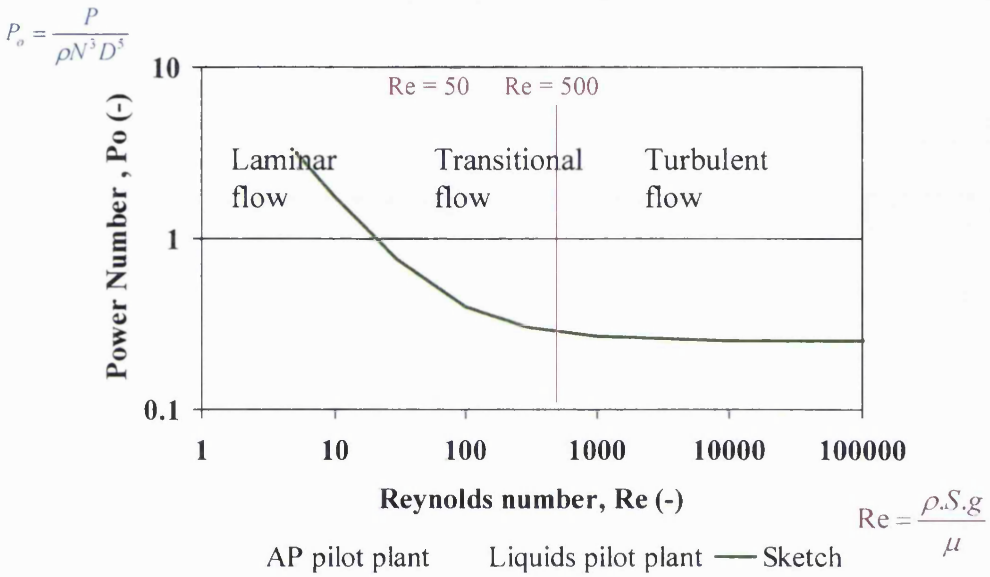


Figure 6.3 : Model of power curve for double screen Silverson homogeniser (reproduced from Baker, 2000)

For the Bentone 38 suspensions it can be calculated that the viscosity that is required to move the flow pattern to the laminar region exists about 130 cP. This suggests that the samples prepared without the polar activator that had very low viscosity (~100 cP) were subject to transitional flow whereas when polar activator was added after a couple of passes through the homogeniser the suspensions moved into the laminar region of flow.

It is possible that there is some extensional shear as the test suspensions enters the rotor-stator gap and is accelerated in a radial direction up to the tip speed of the rotor. Nonetheless the efficacy of break-up in the laminar region is related to shear rate and shear stress. It is therefore reasonable to assume that a shear rate of between 40,000 - 60,000 s^{-1} is insufficient to overcome the energy forces that hold agglomerates of

Bentone 38 together. Increasing the residence time that agglomerates were exposed to the amount of shear in an homogeniser (double screen homogeniser) did not improve agglomerate break down. Basically the particles in the double screen homogeniser are exposed to the same shear rate however they pass through two screens and therefore increase the residency time that they are exposed to the shear rate.

Since the equivalent power measurements to Reynolds number data has not yet been calculated for the single screen laboratory homogenisers it is only possible to assume that the flow through such equipment was equivalent (laminar or transitional). Consequently, the factor that would effect the break up of agglomerates is shear rate through a mixer. This work contradicts the claims made by Kieke (1985) who says that the homogeniser results in turbulent shear. This is true only if the viscosity of the fluid being processed is sufficiently high enough (>1000cP) to increase the Reynolds number. It is feasible however that turbulent shear would enhance the break up of agglomerates since turbulent shear results in inertial and viscous break up.

The Sonolator was the next device to be investigated. The test suspension passes through a narrow slit (0.001-in.). Just behind the slit a blade is positioned that according to the manufacturer, (Sonic Corporation) is brought into an ultrasonic vibration by the fluid motion that causes cavitation in the fluid. The cavitation (a phenomenon in which small gas bubbles in the fluid start to grow until they implode with very high local energy dissipation rates) is then assumed to cause droplet and particle break-up. It is also assumed that the effect of break-up is attributed to passing test fluids through a narrow orifice under high pressure (high shear rates). (Wieringa et al, 1996). The shear rate for Sonolator has been calculated to be in the region of 10^4 to 10^5 s^{-1}. Wieringa and colleagues calculated that the break-up of emulsion droplets is dominated by extensional flow since the residence time droplets experienced far exceeded the shear time through the orifice. However, it is likely that both factors contributed to droplet break- up.

The results of the Bentone 38 samples that had been processed on the Sonolator displayed highly effective particle break down. The samples that contained propylene carbonate were effectively fully dispersed after 5 shear passes through the sonolator. Continued shear passes had no significant increase on product viscosity however, it was impossible to process the gel above thirteen passes since the product gelled in the equipment. The same viscosities were only achievable with the sample that did not contain propylene carbonate after 25 passes. However, this proved that provided sufficient shear was imparted to the Bentone 38 in the absence of a polar activator a structured gel was achievable. From a practical and commercial point of view, this would not be an acceptable manufacturing process (even five passes with a polar activator), however, it did provide evidence that polar activator was not essential to the mechanism of a gel network.

The final shear equipment to be evaluated was a laboratory scale high-pressure homogeniser produced by APV homogenisers. This is currently the most efficient device that has been designed for the breakdown of droplets or emulsification. The high-pressure homogeniser consists of a high-pressure displacement pump and a homogenising valve that works on a 'drop and lift' principle. A spring-loaded valve rests on a flat 'seat' at the end of a tube. During operation, the mixture is pumped at a constant rate to the centre of the seating. This lifts the valve and the mixture passes radially through the slit aperture. The aperture of the slit is difficult to accurately measure although it is understood to be in the range of 15-300 μm (Dickinson, 1994). As homogenising pressure is increased, the valve lift is reduced, the slit width becomes narrower and the resulting droplets become smaller. This technology has been well established for emulsions for reducing droplet size and therefore it was proposed as a potential method for reducing Bentone 38 agglomerates in silicone fluid since a method for effectively delaminating particles had not been established.

It is extremely difficult to measure the dimensions of the gap settings for the homogeniser since they are dependent upon the process pressure at the time of the experiment. Nevertheless, Mulder and Walstra, (1974) calculated that a mixture of laminar and turbulent flow exists and that the transition from laminar flow down the inlet pipe to turbulent flow at the slit entrance occurs at a Reynolds number that depends upon the width and whether the inlet boundary is rounded or sharp edge (Phipps, 1985).

It has been calculated that for large-scale commercial homogenisers, the Reynolds number is well in excess of 10^4 and therefore clearly turbulent flow. It is assumed therefore that the Reynolds numbers for laboratory scale homogenisers, while lower, are still within the turbulent flow range. In the slit itself the flow is believed to be different. The turbulence is probably squeezed owing to the strong convergence of the flow of fluid through the gap. As it passes through the slit, the fluid is subjected to very high rates of strain, both in shear and in elongation. This is why this type of shear is sometimes referred to as extensional flow. Figure 6.4 shows a diagram of the deformation of particles.

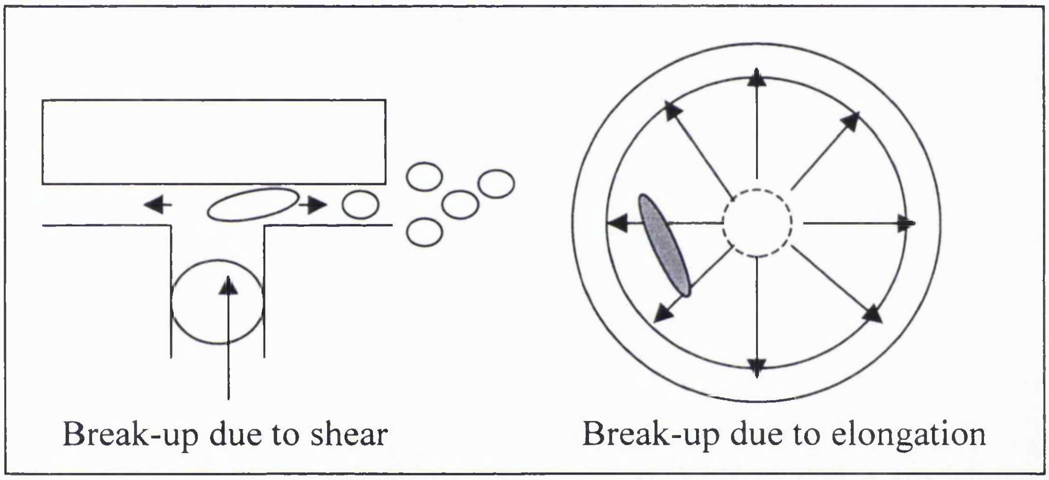


Figure 6.4 : Deformation of particles in high pressure homogeniser

The reason why the high pressure homogeniser was selected for testing with Bentone 38 samples was firstly because it yields the highest shear rates possible in the equipment that was available, but also because of the extensional flow that is subjected to each particle. The theory behind this machine being used to optimally delaminate the clay particles was that the turbulent shear would first disrupt large agglomerates. Then as the particles are forced through the orifice they would be propelled radially out through the narrow gap forcing platelets to be literally ripped away from each other in a lateral direction through laminar shear. Based on an average flow rate of 50 m/s and the dimensions of gap size quoted by Dickinson (1994) the shear rate was calculated to be in the order of between 1.5 – 3.3 x 10^6 s^{-1}.

The second factor that is a consequence of high-pressure homogenisation is that power dissipation in the form of heat is always expended. This heat may also contribute to efficiently delaminate the particles. The loading pressure is first converted to kinetic energy of fluid elements and then into thermal kinetic energy of the molecules. As pressure is increased the amount of energy that is dissipated as heat also increases and this is thought to play a significant role in the delamination of Bentone 38 particles.

The results of the experiments with the high-pressure equipment show that it is possible to delaminate clay agglomerates using high-pressure homogenisation. The higher the process pressure, the more efficient the deagglomeration since shear rate increases and process temperature also rises. It was also possible to create a gel structure in the absence of a polar activator however stability of the gel network was significantly increased when a small percentage of polar activator was added. It should be noted that full delamination of particles was not achieved in the formulation with Bentone 38 and Silicone fluid alone even after four passes at 1000 bar, however the agglomerates were of dimensions that can formed a weak gel. These samples were processed where the temperature of the process was maintained at 13°C by means of a cooling coil to try and reduce the effect of temperature on the process. It is impossible to completely reduce thermal effects through energy dissipation, however the temperature of the process was understood to be below any phase transition that can occur with the quaternary ammonium (50°C). The temperature differential was recorded to be a rise of 20°C during the process and the gel collected was immediately subjected to the cooling coil upon exit from the homogenisation valve.

6.4 Thermal Effect on Delamination of Platelets

The third effect that could contribute to the delamination of organoclay particles is the effect of thermal energy. Initial results of High Sensitivity Differential Scanning Calorimetry showed a definite phase transition occurred for Bentone 38 with a maximum heat flow at approximately 43°C. The phase transition occurred over a range of between 30 and 60°C. This is believed to be due to the fact that Bentone 38 is a commercial grade of organic clay and it is highly possible that the quaternary ammonium is composed of a mixture of alkyl chain lengths with the dominant chain length being C18. This temperature range correlates to the phase transition of octahedral alkanes from L_β to L_α form i.e. from semi solid to liquid. In the presence of silicone fluid and propylene carbonate the peak of the phase transition occurs at slightly lower temperatures (~ 40°C and 38°C respectively). This would imply that the addition of polar activator or solvent does not have a major implication on the solubility of the quaternary ammonium since it would be expected that the peak would not be observed if the compound had already be solubilised. Based on this knowledge, the hypothesis that the organic layer, at ambient conditions, has sticky semi-solid properties, however if the process temperature was exceeded to above the melting point of the alkyl chains, the consistency would be more fluid like and therefore the potential to for plates to slip apart in a lateral direction would be easier to achieve. Using the analogy of glass plates sandwiched together, it is almost impossible to prize the plates apart when a small amount of liquid is present between the sheets due to strong attractive forces unless the two surfaces are forced to slide across each other in a lateral direction. This principle may be applied to clay agglomerates. By melting the quaternary layer between the platelets and introducing a further liquid e.g. through capillary draw, the platelets would require less energy to disrupt the van der Waals forces of attraction that hold the agglomerates together. This, combined with a shear force in a lateral direction experienced in extensional flow has been shown to effectively delaminate clay platelets.

Consequently, a study investigating the effect thermal energy without polar activator was made. The results showed that elevated temperature alone was not sufficient to delaminate particles and this was correlated with the XRD study that showed only a very slight increase in basal spacing was achieved through heating alone. Processing using the medium shear rate Silverson had no structuring benefit and did not result in gel formation. However, when the samples were processed at very high shear rate using the APV Rannie homogeniser at 50°C, the results were dramatic. A highly viscous (>500,000cP TA @ 10rpm) gel was created. The sample that was prepared under controlled ambient temperature using a cooling coil had a product viscosity of 15,000 cP . The gel was observed to be highly stable over a number of months displaying almost no syneresis. The syneresis of fluid was likely to be due to some flocculation of particles and slight sedimentation over time, however it was possible to conclude that a very stable gel had been created without the need of a polar activator.

6.5 Microstructure of Bentone 38 Gel

To investigate the microstructure of this gel the samples were investigated using SEM and cryo-SEM. The micrographs given in Chapter Four (Figure 4.41 – 4.44) clearly show images of untreated Bentone 38 agglomerates and effectively dispersed gel networks that are achieved through optimum process conditions. The microstructure of two gels manufactured (with and without polar activator) appeared identical and had a structure that could be described as being analogous to a sponge. The SEM images of the network appeared to display that the dispersion of particles formed a partially flocculated network.

The following comments can be made regarding the observed microstructure of the gels:

- Firstly, primary clay particles or platelets interact with themselves (through folding) and with each other through particle-particle interactions (edge to edge, face to face and edge to face). It would appear that all types of orientation of platelets are acceptable and there is no formal or rigid configuration noted.
- Secondly, the primary particles appear to form open agglomerates or flocs since domains of connected agglomerates that extend over tens or hundreds of microns were observed. Between these flocs are a network of fluid rich zones, channels or fractures that could be critical in determining gel stability (refer back to Figure 4.44).

From the evidence based on the processing studies, it is apparent that thermal and mechanical energy is critical to developing the microstructure of the gel network. It would appear that the size, shape and distribution of organoclay platelets and agglomerates are a function of the manufacturing process used to produce it. A gelled network was only possible when excessively high shear rate and elevated temperature was applied to the Bentone 38 and Silicone fluid formulation. The shape and ability of the clay sheets to deform means that high stress-flow induced structures will remain intact due to steric resistance to reorientation in such a high phase volume system. In other words, individual particles are locked into place by the mere presence of the surrounding particles.

The process to achieving such a microstructure is thought to be as follows: The raw material, Bentone 38, is broken down to primary particles by extensional flow and very high shear rate exerted by the high pressure homogeniser. Fresh agglomerates are formed as the platelets exit the homogenising valve through deceleration and collision as the pressure returns to normal. These new agglomerates are now open networks and there is no evidence of reagglomeration to the spherical, rock like agglomerates that were observed prior to processing.

The forces that exist for any colloidal suspensions include van der Waals, electrostatic, steric and solvation contributions. Attempts were made to correlate hydrogen bond strength and concentration from different polar activators with gel viscosities (Cody et al, 1986). No correlation was observed. At molecular levels, hydrogen bonds may play a role in an organoclay-based system by affecting the orientation of adsorbed species e.g. the quaternary ammonium species.

The following comments may be made that may contribute to the different mechanisms that create a gel microstructure.

There is strong evidence from these studies that high dielectric constant materials like propylene carbonate will concentrate at the surfaces of organoclay. Once there, the polar molecules may alter the local dielectric constant to such an extent that local ionisation of the adsorbed cationic may take place resulting in the formation of a net negative surface charge. The presence of surface charge in a non-aqueous system presents a number of possible reasons for stable gel network to exist:

- Despite the presence of surface charge, the ionic concentration in the surrounding silicone fluid will be low. The resulting low shielding effect and low dielectric constant of the silicone fluid means that the double layer effect may be extensive. In a fully dispersed system, the concentration of primary particles is high and agglomeration or flocculation will occur as a means to reduce the free energy of the system caused by electrical field overlap. Since the particles are constrained in a container the particles are hindered from repelling each other and moving away and consequently are forced into contact and thus a gel is observed.
- Standard texts report that the edges of clay platelets are positively charged. Also the presence of quaternary ammonium cationic on the surface of the clay creates the potential of ionisation producing absorbed positively charged sites. The presence of both negative and positive charges would inevitably contribute to flocculation and agglomeration of particles. This is not believed to be a dominant factor in the observed microstructure.
- Once particles come into close contact, short-range van der Waals forces would become important that would hold solid surfaces together. Formation of hydrogen bonds may also contribute to the structure once surfaces are in contact.
- Surface charge may however be immaterial with flocculation resulting from fluid mechanical factors such as orthokinetic (agitated) agglomeration where coagulation of particles is observed. The subsequent structure may then be retained through simple steric factors.

CHAPTER SEVEN

CONCLUSIONS AND FUTURE RECOMMENDATIONS

7.1 Conclusions

The overall objective of this research was to study the mechanism of creating a structured organophilic gel and to determine its microstructure based on the information that the organoclay (Bentone 38) naturally forms agglomerates that must be delaminated in order to form a network structure. Through a matrix of experimental procedures that investigated mechanical, thermal and polar effects on the structuring of Bentone 38 in Silicone fluid the following conclusions have been drawn:

- The role of the polar activator was found to influence the clay suspensions though an increase in base viscosity but did not yield a stable gel when processed using the recommended process procedure (standard laboratory/pilot plant homogeniser, shear rate 40-60,000 s^{-1}) in the literature (Rheox Ltd).

- Optical microscopy has shown that standard laboratory homogenisers did not have sufficiently high shear rates to delaminate clay particles even with repeated shear passes, processing at elevated temperature or in the presence of polar activators.

- The study provided evidence that the polar activators gave a ranking in order of efficacy to increasing base viscosity with propylene carbonate being the most efficacious. There was no correlation to the size of the polar activator molecule, dipole moment or functional group with regards to efficacy of polar group.

- Effective delamination of Bentone 38 agglomerates in silicone fluid does not require the presence of a polar activator to swell the platelets provided a sufficiently high shear rate is applied (10^5-10^6 s^{-1}). This was only achieved using a very-high pressure homogeniser at process conditions of in excess of 1000 bar or a high shear Sonolator after numerous shear passes (>20 shear passes).

- Polar activator does not significantly reduce the shear rate that is required to delaminate the particles since it was found that delamination of platelets only occurred at very high shear rates. The study did however show in the Sonolator and high-pressure Rannie Homogeniser experiments that the overall residence time of shear may be reduced when polar activator is present.

- Temperature was shown to play a significant role in the delamination of clay platelets when the organoclay was processed at very high shear rate using the high-pressure homogeniser. High Sensitivity Differential Scanning Calorimetry provided evidence that the quaternary organic group underwent a phase transition between 30-50°C that correlates to the transition of the hydrocarbon chains undergoing a transition from the L_β to L_α phase. The melting of the quaternary group on the surface of the clay was concluded reduce adhesive forces and to aid lateral slip between the platelets when extensional shear was applied.

- The most stable gel network was produced when both very high shear mechanical energy and thermal energy was applied in the presence of a polar activator. It can therefore be concluded that a gel network cannot be attributed to one element but that the mechanism for delamination of agglomerates is a highly complex procedure that requires a combination of processing factors.

- This study concludes that the critical factor to optimally dispersing clay platelets is the shear rate and flow dynamics of the processing procedure and not the presence of polar activator. Polar activator does enhance overall product stability but a stable gel may be formed without polar molecules provided the gel is processed at a temperature that is above the melting point of the quaternary ammonium compound and extensional high shear is applied. It would appear that swelling of particles does not contribute as greatly to the mechanism of delamination of platelets as suggested in the literature sources. Consequently, it can be concluded that the mechanism for structuring organoclays proposed by Rheox Ltd (Figure 6.1, Scheme (a)) is not ideal. The schematic mechanism proposed in this research (Figure 6.1, Scheme (b)) recommended that the adhesive forces between clay platelets must be overcome through lateral and very high extensional shear rates. It is this process that results in the effective delamination of clay platelets but the addition of thermal energy and or polar activator that aids gel stability.

- This study found that visualising the microstructure of the gels by cryo-SEM was not a simple matter and required a specific rationale for cryogenic sublimation of the silicone fluid to enable a realistic picture of the network to be recorded. This is expected to be different for each different type of non-aqueous solvent and therefore it would be concluded that for each new type of sample to be viewed, an evaluation of sublimation time and temperatures should be performed.

- Cryo-SEM displayed that the microstructure of Bentone 38 gels consist of an open structure of distorted (non-planar) sheet like clay particles. The cryo-SEM images in Chapter 4 show that this open network forms very loose agglomerates however, these do not form the closely packed agglomerates of the raw material Bentone 38 (also imaged in Chapter 4) prior to being processed.

- Open-network agglomerates occupy the majority of the phase space and it is assumed that the silicone fluid accumulates in the irregular channels that interconnect the platelets. The network resembles a sponge-like appearance and it is concluded that the silicone fluid is held between the voids of the network through capillary forces.

- Throughout this study a number of mechanisms have been postulated to account for the gel network dispersion. This study indicates that the microstructure of Bentone 38 clay gel is a result primarily of steric hindrance of platelets due to optimised dispersion through a high shear process. The addition of a polar activator is most likely to contribute to stabilising the gel network through localised charging of platelets and their intimate contact moving the particles into van der Waals contacts. Effects of hydrogen bonding may also contribute partially to the structure although it was not possible to make conclusive remarks regarding this matter.

7.2 Future Recommendations

This research has enabled an insight into how an organoclay gel is generated and has indicated the critical stage in achieving a gel network is the selection of the correct processing parameters. It has indicated that thermal effects play a very significant role in delaminating particles and has also shown that polar activators do not appear to be the catalyst to deagglomeration.

There are still many unknowns in this field of study that need to be developed further. For example, the true role of the polar activator still needs to be defined. In order to assess the true potential of the polar activator, a significantly wider range of activators should be evaluated. This selection should include activators with common functional groups and their chemical analogues. The recommended process procedure would be to process gels using high-pressure homogenisation (>1000 bar) to ensure full delamination of clay platelets. This would result in stable gel manufacture and thus enable the rheological properties of these gels to be evaluated in greater detail and thereby enable further insight into the product microstructure.

The effect of the quaternary group could also be evaluated further by evaluating a range of different organic coatings, both commercially available and by coating with purified and chain length specific hydrocarbons quaternaries. This would provide information on compatibility with silicone fluids and other non-aqueous liquid phase substances.

Electrophoretic studies could be further utilised to determine the optimum properties of a polar activator and investigate the effects of blending polar activators e.g. a good swelling agent plus a good dispersant that could enhance the gelling properties of clays.

Further understanding into the forces that exist between clay platelets would be enhanced if a method for coating mica sheets with the organic molecule could be optimised. This would identify whether repulsive forces exist between organophilic clays and would give a greater insight into adhesive forces in the presence of polar molecules.

In addition, a greater understanding of the polar activator interaction with the cationic compound would be enhanced through solubility studies. Wetting behaviour of the clay surfaces could also be investigated by measuring the contact angle of these systems and further investigating surface tension.

The effects of swelling of clay platelets through X-ray diffraction work could also be investigated in conjunction with Neutron Scattering studies. By tagging the quaternary ammonium compounds at specific sites on the hydrocarbon chains and evaluating the compounds with Neutron Scattering would enable an insight into structural positions. This could be complemented with the introduction of thermal effects and polar activators to determine whether there are steric changes as a consequence.

The processing studies could be further investigated by evaluating different processing regimes. The Silverson homogeniser was found to be unsuitable for delaminating clay particles despite the laminar flow and extensional flow that is generated across the rotor stator gap. It is possible that more effective delamination would have occurred if the system had been subjected to turbulent flow. One possible route to achieving this would be to prepare a highly concentrated and viscous formulation that would increase the Reynolds number and move the system to the turbulent flow region. This may improve the delamination of platelets to effectively disperse the clay. The system could then be diluted with the remaining solvent to complete the formulation. In addition, further investigation into determining the effect of residence times within the gap could also be investigated to determine whether shear rate could be reduced to a more generally practical method.

Processing studies could be developed further by determining the effects of different dimension orifices on gel networks. The different process equipments used in this study were designed originally for reduction of droplet size in emulsion type products and the theory to reducing droplet size were applied to deagglomerating powders. With the knowledge that lateral and extensional flow at high shear rates is paramount to effective delamination, there is scope to design specific homogenisation valve assemblies and orifices to optimise the delaminating process. Further work could also be applied to determining the effects of flow rate on particle size reduction and into gaining a greater knowledge on the effects of turbulent and laminar flows.

The microstructure of clays is hypothesised to be due to steric effects and further work into determining the surface interactions of clay platelets could be also evaluated. Production of different formulation clays with polar activators, anhydrous systems alternative organoclays could provide further information into microstructure that has been imaged to date.

APPENDICES

Appendix 1.1

Chemical X-Ray Fluorescence (XRF) Spectroscopy Analysis of Bentone 38 Clay – Laboratory Analysis

Element	%
Na_2O	0.3
MgO	30.9
Al_2O_3	1.3
SiO_2	63.9
P_2O_5	0.4
S	0.05
Cl	0.6
K_2O	0.3
CaO	1.6
TiO_2	0.04
MnO	0.01
Fe_2O_3	0.5

Table A : The chemical analysis of trace elements of Bentone 38 clay using XRF.

XRF technique provides an indication of the inorganic content of the Bentone 38 clay. The percentage of magnesium oxide and silicon dioxide in the sample of Bentone 38 clay provides evidence of a 2:1 ratio confirming that the sample is dimorphic. These two elements also predominate in the chemical composition of the clay confirming that the clay is a hectorite. The presence of trace elements in the specimen is a result of isomorphous substitution and account for the electrical surface charge of the clay.

Appendix 2.1

Additive	Rating
Nitromethane	1.02
Propanone	1.00
Nitroethane	0.95
Propylene Carbonate	0.94
Acetophenone	0.90
Ethylene Carbonate	0.90
Methyl Ethyl Ketone	0.86
Methanol	0.79
Ethanol	0.75
Propanol	0.68

Acetone = 1 (benchmark)

Table B : Polar Activator Efficiencies in Order of Rating
(Reproduced from NLGI No 2)

Appendix 2.2

Typical Parameters of Rheological Flow Profile (Carri-med)

Cone and Plate

Geometry name:	concentric cylinders
Stator inner radius (R2) (mm):	24.00
Rotor outer Radius (R1) (mm):	19.00
Cylinder immersed height (mm):	24.50
Required gap (micro m):	3000
Inertia (micro N.m.s^2)	1.050
Material:	steel
Solvent trap:	no

Procedure name:	Flow experiment
Step name:	Pre-experimental step
Perform step:	yes
Initial temperature (Deg C)	25.0
Wait for correct temperature:	yes
Perform preshear:	no
Preshear variable:	shear stress
Applied value (Pa):	0
Preshear duration (HH:MM:SS)	0:00:00
Perform equilibration:	yes
Equil. duration (HH:MM:SS):	2:00:00
Wait for Zero velocity:	yes

Step name:	up curve
Perform step:	yes
Step type:	stepped ramp
Temperature (Deg C):	25.0
Controlled variable:	shear stress
Start value (Pa):	0.3
End value (Pa):	5.00
Ramp mode:	log
Number of points:	30
Constant time (HH:MM:SS):	0:00:10
Inv. proportional time:	0
Wait for equilibrium:	yes
% tolerance:	1.0
Max. point time (HH:MM:SS)	0:45:00
Consecutive within:	2

Typical Parameters of Rheological Flow Profile (Carri-med)

Vane and Basket

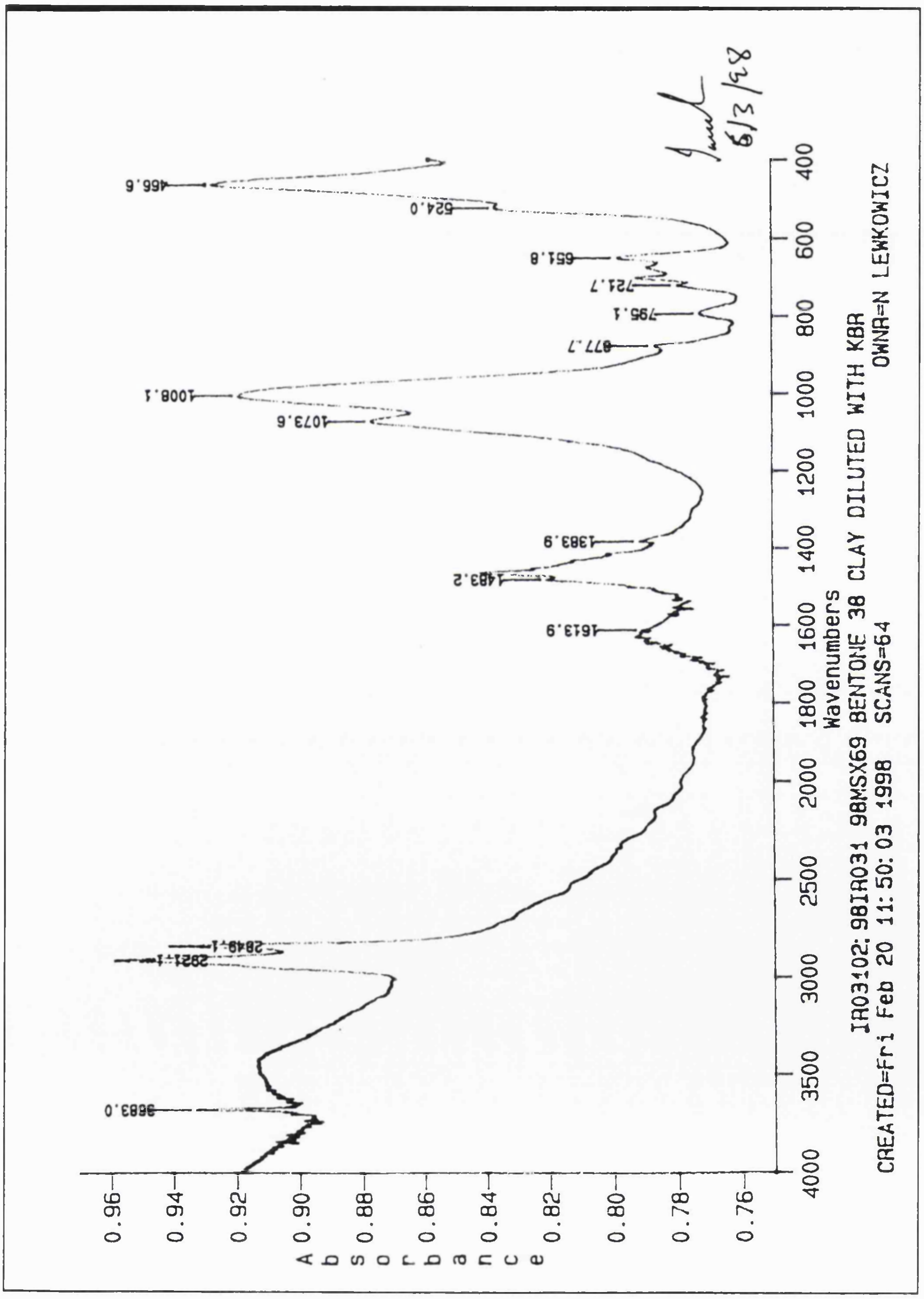
Geometry name:	concentric cylinders
Stator inner radius (R2) (mm):	12.00
Rotor outer Radius (R1) (mm):	10.00
Cylinder immersed height (mm):	20.00
Required gap (micro m):	3000
Inertia (micro N.m.s^2)	1.000
Material:	steel
Solvent trap:	no

Procedure name:	Flow experiment
Step name:	Pre-experimental step
Perform step:	yes
Initial temperature (Deg C)	25.0
Wait for correct temperature:	yes
Perform preshear:	no
Preshear variable:	shear stress
Applied value (Pa):	0
Preshear duration (HH:MM:SS)	0:00:00
Perform equilibration:	no
Equil. duration (HH:MM:SS):	0:00:00
Wait for Zero velocity:	yes

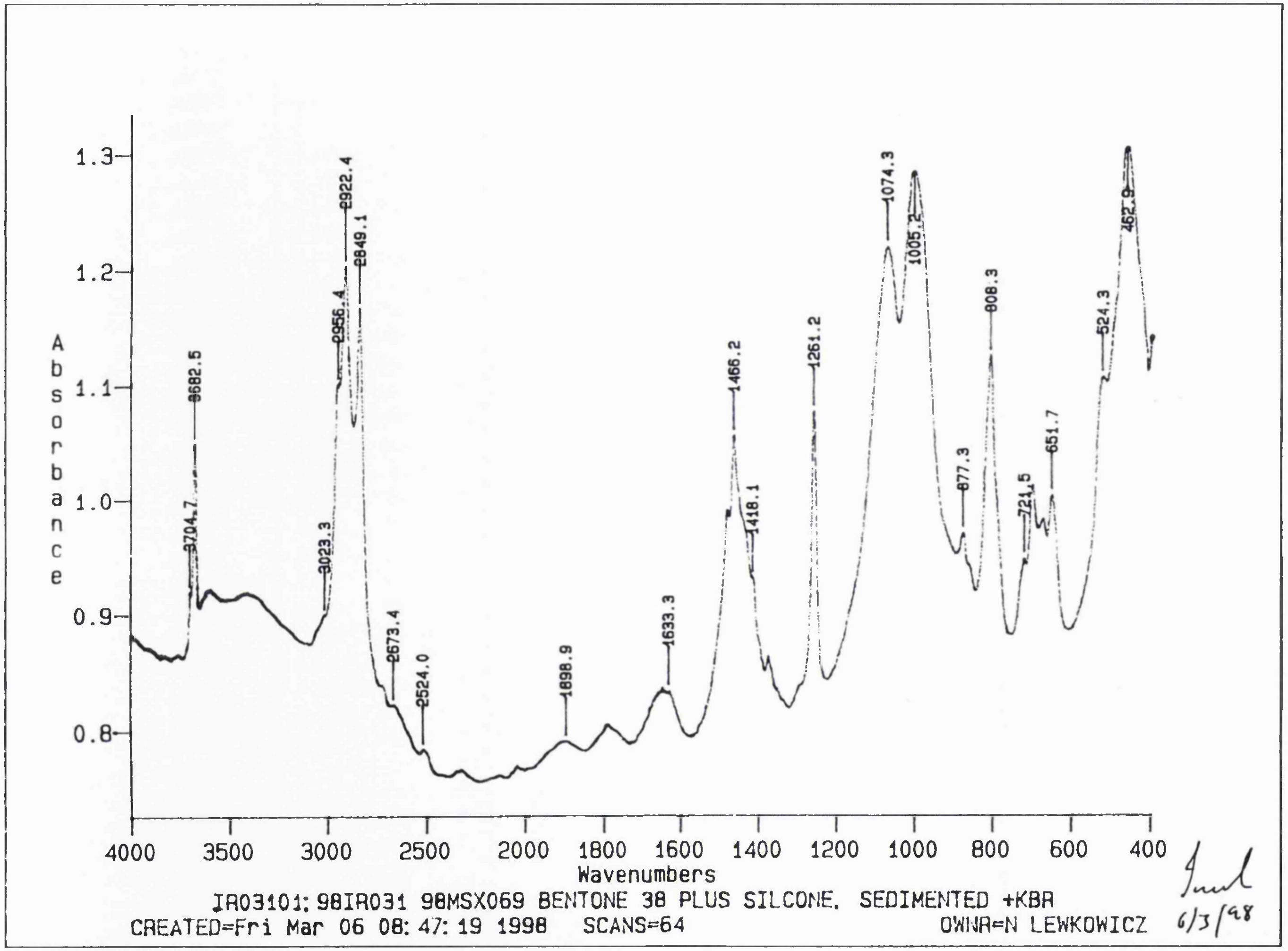
Step name:	up curve
Perform step:	yes
Step type:	stepped ramp
Temperature (Deg C):	25.0
Controlled variable:	shear stress
Start value (Pa):	0.1
End value (Pa):	30.00
Ramp mode:	log
Number of points:	25
Constant time (HH:MM:SS):	0:00:10
Inv. proportional time:	0
Wait for equilibrium:	yes
% tolerance:	1.0
Max. point time (HH:MM:SS)	1:00:00
Consecutive within:	2

Appendix 2.3

Infra-red Spectra of Bentone 38 and Bentone 38 + Silicone Fluid



Infra-red Spectra of Bentone 38 and Silicone Fluid



IR03101; 98IR031 98MSX069 BENTONE 38 PLUS SILCONE. SEDIMENTED +KBR
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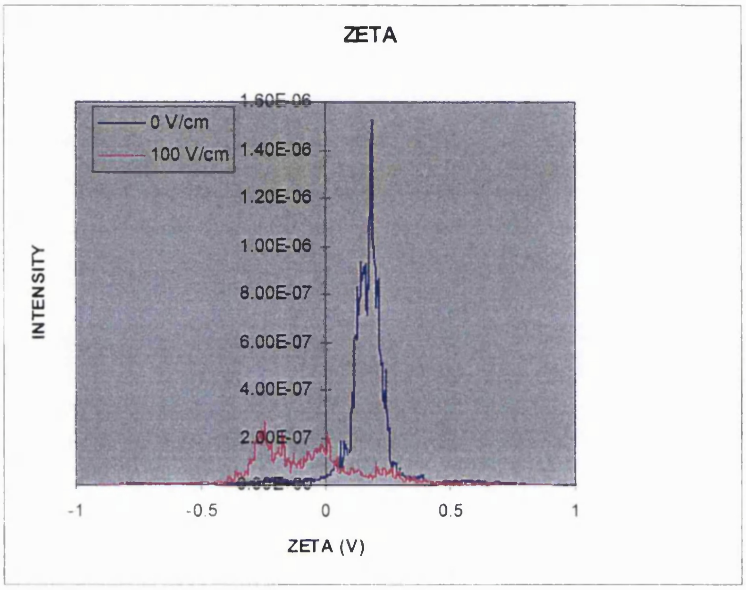
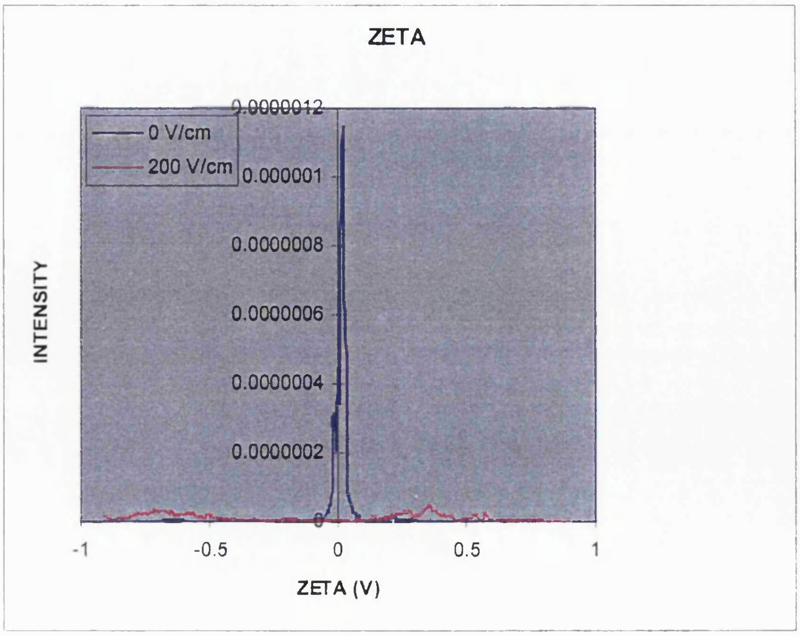
6/3/98

Appendix 3.1

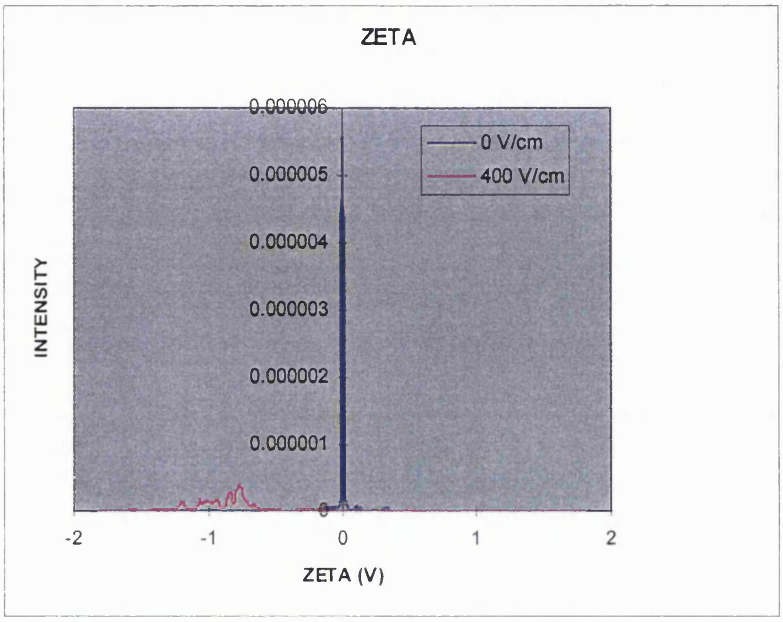
Further experimental data for Propanone Electrophoretic Studies



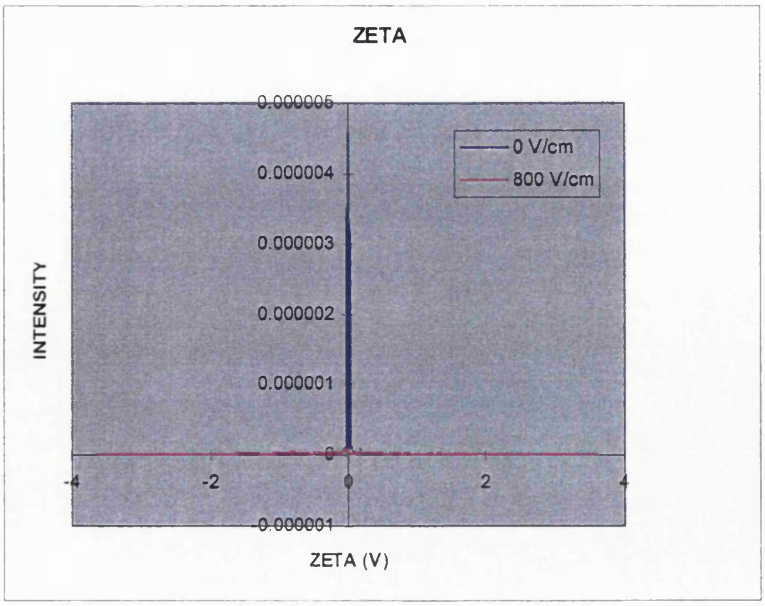
Electrophoretic mobility data : 10% propanone dispersion; field = 100 V/cm



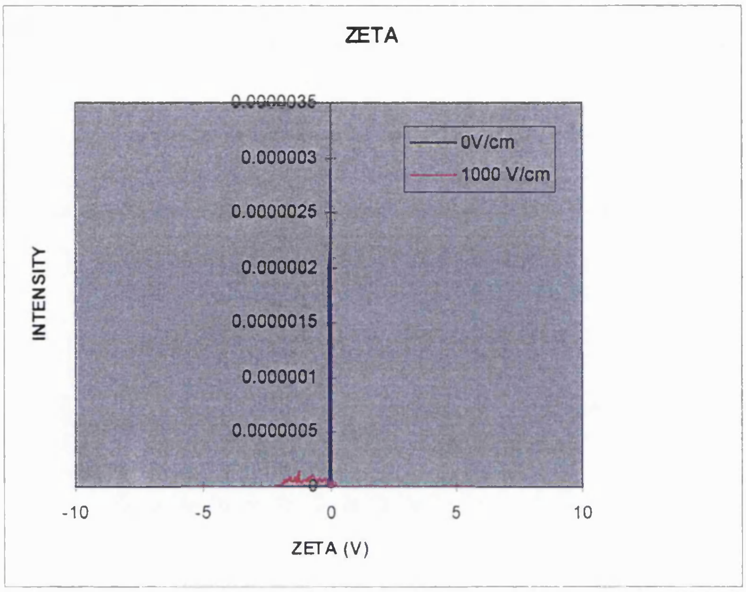
Electrophoretic mobility data : 10% propanone dispersion; field = 200 V/cm



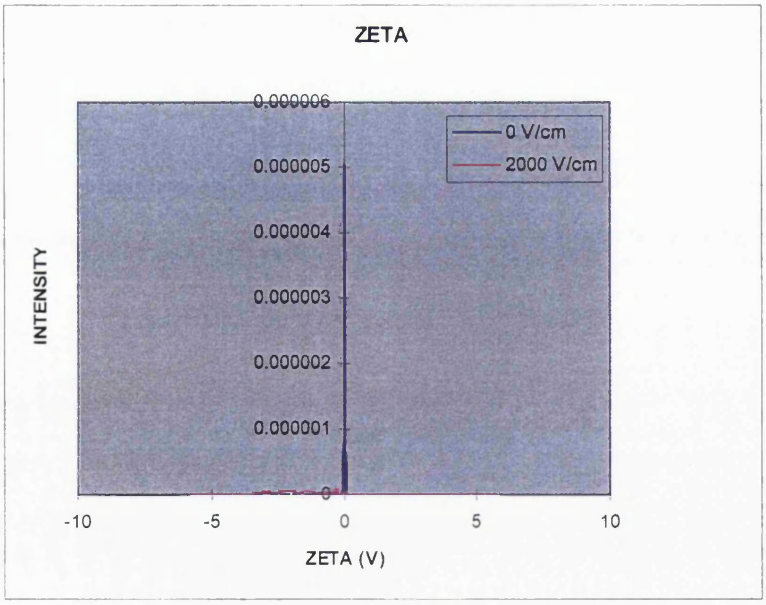
Electrophoretic mobility data : 10% propanone dispersion; field = 400 V/cm



Electrophoretic mobility data : 10% propanone dispersion; field = 800 V/cm



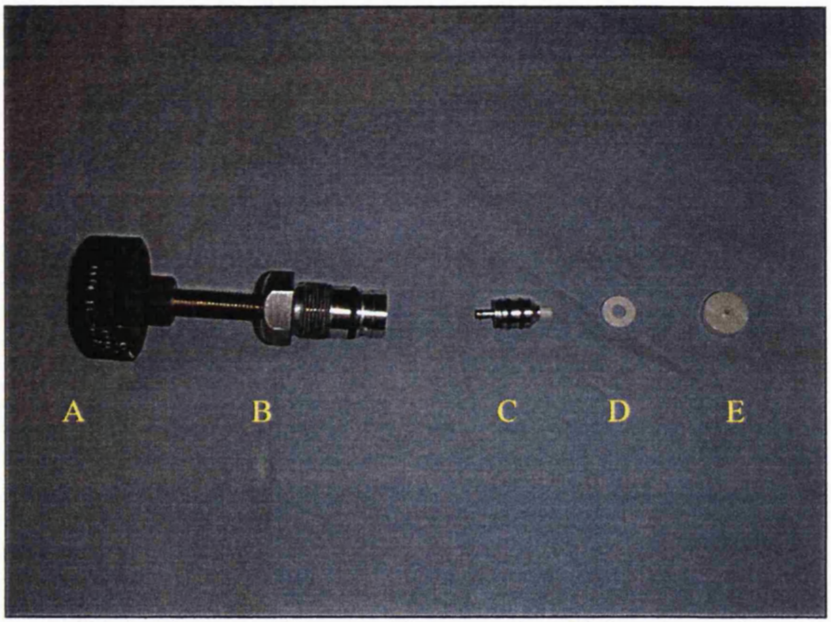
Electrophoretic mobility data : 10% propanone dispersion; field = 1000 V/cm



Electrophoretic mobility data : 10% propanone dispersion; field = 2000 V/cm

Appendix 4.1

Description of Homogeniser Valve Assembly



Digital Image of Rannie Homogeniser Valve Assembly

The Homogenising valve assembly comprises:

A	Handwheel
B	Guide
C	Valve Socket
D	Impact Ring (ceramic)
E	Bottom Part (ceramic)

The Valve socket, impact ring and bottom part are encased in the stainless steel guide. The valve is adjusted by means of the handwheel. A flow through the valve must first be initiated to float the bottom part in the chamber. Once flow has been established, the handwheel is turned slowly in a clockwise direction to lower the valve socket and impact ring to generate a gap between the ring and the bottom part. A spring is located within the guide to maintain a constant gap. High pressure is a result of the fluid being pumped through the valve at a constant flow rate and is proportional to the gap width.

Appendix 4.2

Soxhlet Extraction Experimental Detail

1. Bentone 38 clay (5g) was weighed into an extraction thimble (30mm x 100mm). The thimble was stoppered with a plug of cotton wool and placed inside a soxhlet condenser.

2. A mix of 60:40 chloroform : methanol mix was prepared. The mix (200ml) was poured into a dessicated flat bottomed flask containing 4 glass beads.

3. The soxhlet condenser was connected to the flask and then to a water condenser and placed on an isomantle.

4. The flask was swirled intermittently until the mix was boiling to prevent superheating and pressure build-up. The mixture was left to reflux for 6 hours.

5. The soxhlet equipment and contents were left to cool. The water condenser was then switched off.

6. The solvents were distilled off using a steam bath until approximately 10ml of the solvent extracts remained.

7. The solvent extracts were retained and the remaining clay in the thimble was analysed using XRF for trace element content. The remainder of the clay was reserved for HSDSC studies (unhydrophobed reference sample)

Appendix 4.3

A. Calculation of Shear Rate of In-Line Silverson Lab Scale Homogeniser

By determining the dimensions of the stator and rotor of the Silverson and using a rev. counter it was possible to calculate the amount of shear that was applied to the mixture at a given speed. The method for how this was performed is shown below:

A piece of black tape was fixed around the shaft of the in-line Silverson Mixer. A small square of silver tape was positioned over the black tape. The mixer and tubing was primed with Silicone Fluid 1465 (Dow Corning) ensuring that the head was free from air bubbles. The fluid was recirculated through the in-line Silverson at constant flow rate via the peristaltic pump. Using a portable rev counter (TM 4010 Line Seiki) rpm readings were taken by shining a constant beam at the tape. The instrument measured the number of times the beam was broken each time the silver square came into the field. Measurements were taken for each speed setting on the Silverson by ramping the speed until maximum was reached. Silverson Machines Ltd. recommends that the In-Line mixer arrangement should always be run at maximum speed. The geometry dimensions of the stator and rotor were measured using instrument callipers.

The table below gives the results of the speed measurements of the Silverson Mixer taken throughout the experiment. The experiment was repeated to ensure validity of results

Silverson Speed Setting	**Speed (Ramped) / rpm**
0	7582
1	7563
2	7691
3	8001
4	8216
5	8461
6	8762
7	9276
8	9818
9 (max.)	9823

Table C : Shaft speeds (rpm) of Silverson In-Line Lab Scale Homogeniser

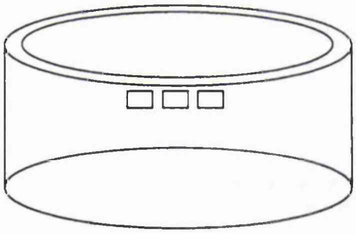


Diagram of Stator

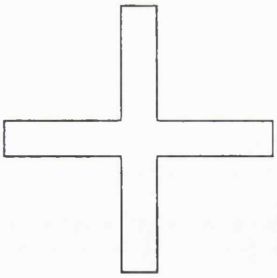


Diagram of Rotor

Dimensions of Geometries

Dimension of Rotor = 31.115 mm

Dimension of inner surface of Stator = 31.65 mm

Dimension of outer surface of Stator = 34.84 mm

Shear Rate Calculation

$$\text{Gap} = \frac{(\text{Dimension of Inner Surface of Stator - Dimension of Rotor})}{2}$$

$$\text{Gap} = \frac{(31.65-31.115)}{2}$$

Gap = 0.2675mm = 0.26 x 10^{-3} m^{-3}

Circumference of Rotor :

C = πD

C = π 0.03165

C = 0.099 m

Distance travelled by Rotor at Maximum Speed :

D = 9823 x 0.099

D = 976.7 m

Velocity :

$$V = \frac{976.7}{60}$$

V = 16.28 ms^{-1}

Shear Rate :

$$\dot{\gamma} = \frac{16.28}{0.27x10^{-3}}$$

$$\dot{\gamma} = 60{,}296 \ s^{-1}$$

∴ Maximum shear rate for the In-Line Silverson L4R is 60,000 s^{-1} @ 9823 (max. speed)

B Calculation of Shear Rate for Pilot Plant Double Screen Silverson

The same calculation may be used to determine the shear rate of the pilot scale homogeniser. The following measurements were taken to enable the calculation:

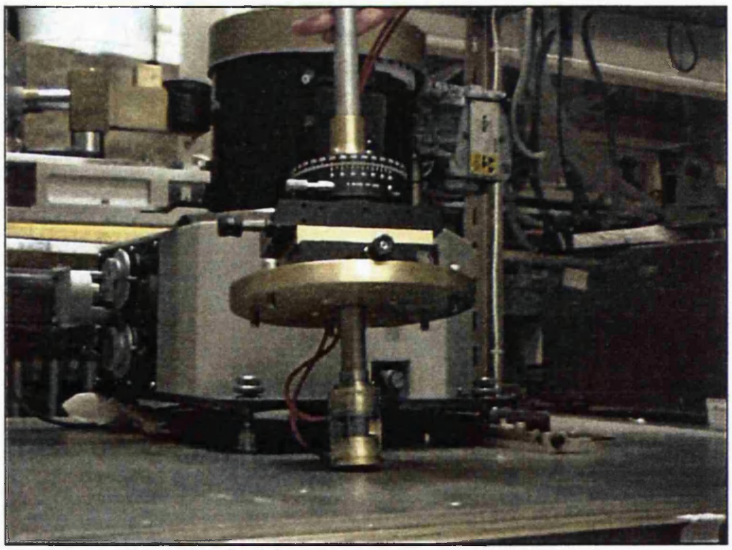
Gap = 0.4 mm
Rotor diameter = 63.2 mm
Speed of rotor = 5000 rpm

Shear rate of pilot plant 30 kg double screen silverson = 41,364s^{-1}

Appendix 5.1

Digital Images of X-ray Diffractometer (Oxford University, PCL)

Digital Image of X-ray Diffractometer



Digital image of sample chamber

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