Observations of phase separations in synthetic clays

Table of content

1 Introduction

1.1 Clay suspensions

Through this project I have been trying to get a deeper understanding of some clay suspensions and the changing properties of them when the consentration of salt are changed. The clay which I have been studying are sodium fluorohectorite. My first experiment the spring 1999 was quite successful and made it easy to continue with further investigation of the system in the autumn 1999.

One interesting aspect with the research of clay structures and clay physics are the unlimited possibilties. This scientific field are far from discovered, and one can find new unsolved problems whereeever one starts to look. The former work on clay and studies of phase shifts in clay are therefore mostly dedicated to observations, and was started already in 1938 when I. Langmuir discovered a macroscopic phase separations in natural clay gel [12] . Very few theoretical studies have been made successfully, since L. Onsager as the first scientist gave a theoretical work on this topic [1] . He proved there should exist a nematic phase in a system consisting of two dimensional hard plates.

Following the observational tradition, this report generally asks more questions than answering them, and the report contains quite a few pictures from observations that I have been doing. The work has taught me that a lot of basic work has to be done before some scientific facts can be stated. This report and the experiences I have reached will therefore be a foundation for my following work with the diploma thesis, where a major aim will be to search for more information about the size distributions of the clay aggragates that exist in the samples I have prepared

Finally I would like to explain the use of some words in the report. The careful reader will discover that the terms clay *suspensions*, *dispersions* and *sols* are used appearantly without any system. This is somehow right. A dispersion indicates a solution where some particles are dilluted in a solvent, and is the most general term. A sol or a *colloidal suspension* are often classified as a solution where the particles are less than 1µm. When the particles are bigger than 1µm it is common to call the dispersion a suspension [11] . The difference between these to terms are as one can see hard to overhold since one often finds clay dispersion with particles of different size. I have not paid much attention to this problem, but it is notation to be aware of.

1.2 General work

As mentioned the project work also has contained a lot of ordenary labaratorium work, which has given me experiences far outside the clay subject. I have been dealing with different sorts of salts and acids, which have taught me alot of general lab safety and why it is valuable to plan the work thoroughly before starting.

Another project a did some work on that are worth mentioning is my cooperation with Bernt Førre and the work on designing a temprature controller for a røntgen scattering experiment on dried clay samples. Since my work finally was dedicated to observations of phases in synthetic clay instead I could not finish this mission, but my knowledge about temprature measurements and microprosessors was dramatically aproven.

2 Theory

2.1 Introduction to clay

In this part there will be a short introduction to a traditional view of clay. During the last centuries there has been great interest in clay for different geological reasons. I can not fail to mention an incident in the neighborhood from my child home. In 1893 there was a vast clay avalanche in Verdal. Many people were killed, and the whole community were distroyed. Accidents like this one has occured several places in Norway since there are lots of clay sediments caused by the last glacier period.

A geologist would probably classify clay as the smallest soil particles, accordig to Attenbergs scale; particles with a dimensions less than 2μm. This is however not satisfactory for a physicist, and it is disirable to find a more accurate definition. The clay particles are more generally classified as colloidal particles, and in the colloidal chemistry one finds a definition, for instance by P. Mørk[4] . A colloidal particle is a particle whose dimension in at least one direction is within the range 1nm to 1μm. The other dimensions may also lie within this limit but it is not a necessity.

The clay minerals may be divided into three different groups related to shape: *flakes*, *laths* and *needles*. The groups have differences in scales in different directions, and the one that is studied in this report is the flake shape which have equal dimensions in two direction and another much smaller in the third. Both hectorites and montmorillonites are flake structures.

2.1.1 Smectites

When the platelets are piling up like a pile of cards, some clay minerals, called swelling clays, are able to absorb water between the platelets. The clay minerals that I have consentrated about in my project work , *fluorohectorit*e and *montmorillonite*, are swelling clays. A subgroup of these minerals are the *smectites*, and are clay minerals with a moderate charge per unit cell . The smectite clays are classified in different ways depending of the author. While Velde [9] states that the charge of a smectite unit cell is between 0.2 and 0.7 e^-, Kaviratna [8] define smectites in the range between 0.4 and 1.2 e^-. From Table 2–1 we can see that only montmorillonite satisfies the limits set by Velde, but I will still classify the fluorohectorite as a smectite.

Table 2–1: Unit charge of clays

Clay mineral	Unit cell charge, e^-
Fluorohectorite	1.2
Monmorillonite	0.6

2.1.2 The clay platelet

The clay platelets discribed here have a shape as Figur 2–1. The thickness of the flake is about 10Å, and they have a surface charge dued to the chemical construction inside the platelet. The dimension of the platelet can be different dependent of the clay, for instance is the fluorohectorites suggested to have a diameter of about 20000Å while the size of the clay laponite is only about 200Å.

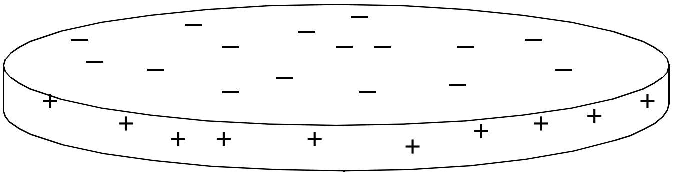

Figure 2–1: The figure shows a clay platelet. The plane surface are negativly charge while the edges have a small positive charge.

The structure of the clays that are studied here are like a sandwitch structure, which are a reason why they are called *2:1 structure* clays. The platelet consist of one octahedral structure between two tetrahedral silica structures. The tetrahedral structure are one silicon atom surrounded by four oxygen atom. These are interlinked through three of the oxygen atoms called basal oxygens. The fourth vacant oxygen atom in the tetrehedral unit cell is called the apical oxygen, and link the tetrahedral sheets to the octahedral structure. The octahedrals are connected the tetrahedrals from both sides through apical oxygens. The octahedral polygon consist of one cation surrounded by six oxygens or hydroxyl groups. The differences in the clay minerals are dued to the fact that both the silocon atoms in the tetrahedrals and the cations in the octahedrals may be exchanged. The most common over all in the tetrahedrals are Si, but also Al and sometimes Fe^{3+} are possible substitutions. The cations in the octahedral are however more various. Al, Mg, Fe^{2+} are most common but species as Fe^{3+}, Ti Ni, Zn, Cr, Mn and Li are found most often.

The fluorohectorites which are studied here, origin from an exchange of Li atoms in the octahedrals instead of Mg. Another significant feature is that all the hydroxyl units are exchanged by F^- ions.

2.2 Forces and potentials ruling the clay suspension

2.2.1 Van der Waals force.

The phenomenon of flocculation in a clay sample demonstrates the existence of some attractive forces in the clay sol. Apparently there are ionic forces interfering among the platelets representing repulsive forces since the charge are not equal to zero. Obvious these ionic forces must be of comparable range and magnitude of some sort of attractive forces to balance and to create a stabilized flocculated phase.

The origin to this attractive force is thermal fluctuations in the electronic configurations in the molecules, known as van der Waals attractions [6,11] . Intantaneously induced dipoles dued to the displaced charge distribution induces dipoles in surrounding molecules in such a way that they attract eachother. At first sight it is not likly that the van der Waals attraction is far-reaching or strong enough to resist the repulsive ionic forces, since they decay rapidly in distance. However, a lot of molecule pair add together and the net sum of all dipoles is sufficiant and creates together with the repulsive potential a stable minimum where the particles can flocculate (See the chapter «DLVO theory»). The force between Molecule dipoles falls as d^{-7}, where d is the distance between them. This yield that the van der Waals force is decreasing very fast and is effective just through small distances.

An important fact to note is that the van der Waals attraction is almost independent of the charge distribution of the surrounding substance, i.e. the solvent, which means that the attractive forces in the clay suspension when adding counter ions are unchanged. The effect of this will be more thoroughly explained in the next chapters.

2.2.2 Double layer theory

The clay platelets are charged, and to balance this some *counterions* must be apparent in the dispersion. The counterions are ions with opposite charge of the platelets. In the experiments with fluorohectorite the platelets are negatively charged, so the counterions are positive. Now the charge of the platelets will influence the distribution of the counterions close to the surface. Some of the counterions are bound to the surface, called a *Stern* or *Helmholtz* layer, some others form an athmosphere close to the surface. This closeup charged layer is known as the electric double layer, and is very important for the behaviour of clay suspensions when ions are added.

This report is not consentrating on the details with regards to the double layer, but an interested reader may well study the theory more rigorously in *Intermolecular & Surface Forces* by *Jacob Israelachvili* [2] or study Simen Lutnæs' projectwork from 1998 [3] .

2.2.3 DLVO theory

Different theoretical work based on experiments have resulted in some theories trying to discribe the behavior of a clay suspension. A famous one, which I will point out in this report is the DLVO[1] theory. This theory combines the attractive forces between the platelets such as

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[1] Dejarguin & Landau 1941 and Verwey & Overbeek 1948

the van der Waals forces, represented by a negative potential U_A, and the repulsive forces regarded to the charge of platelets, represented by a positive potential U_R. The algebraic sum of the two potentials induces the net force between the platelets.

Figure 2-2 shows the contributing potentials and also the net potential. In the graph labeled b) the colloid particles most likely will be trapped in the potential well at about 5nm, since the energy here is lower than for platelets further apart from eachother. If they get even closer however a lower potential is reached, but there exist as we can see a potential barrier in between. To pass this barrier the particles must have enough thermal energy. In this case with a rather tall barrier, they will not be able to pass, and they will stay in the second minimum of the potential. This is called floculation [4] in colloidal chemistry. The attractive and repulsive forces creates a potential well together, that force the clay platelets to stick together within a constant distance, in this case 5 nm. The stability of this phase is dued to the depth of the well, an the heigth of the barrier between the second and the primar minimum. Now if the barrier is smaller, as graph c) and below the size of *kT*, the particles are able to pass and coagulate in the primar minimum.

The van der Waals forces are constant forces between the platelets independent of the amount of salt diluted in the dispersion. The repulsive double layer potential however is strongly influenced by this parameter. The net potential is therefore also strongly dependent of the salt consentration. From the figure we can see that the more salt diluted, the more of the potential looks like the single van der Waals potential. This indicates that the counterions in some sense screen the electrical double layer.

An important parameter dued to the thickness of the double layer is the Debye length Λ, which is the inverse of the more familiar Debye constant:

$$\kappa = \left(\frac{\sum_i \rho_{\infty i} e^2 z_i^2}{\varepsilon k T} \right)^{\frac{1}{2}} m^{-1}, \qquad [2.1]$$

where ρ_i is the bulk number density of ion no. i, e is the unit charge, z_i is the valence of ion no. i, ε is the permability, k is Boltzmanns constant and T is the absolute temperature of the system. We can see that the Debye length is very sensitive to the valence of the counterions in the dispersion since the valence is squared. If there is coexistence of several ions with different valence, the ions of highest valence is influencing more relativly speaking.

The Debye length depends solely on the liquid and are not influenced at all by any of the properties of the surface. In Table 2–2 the Debye length are calculated for three different elec-

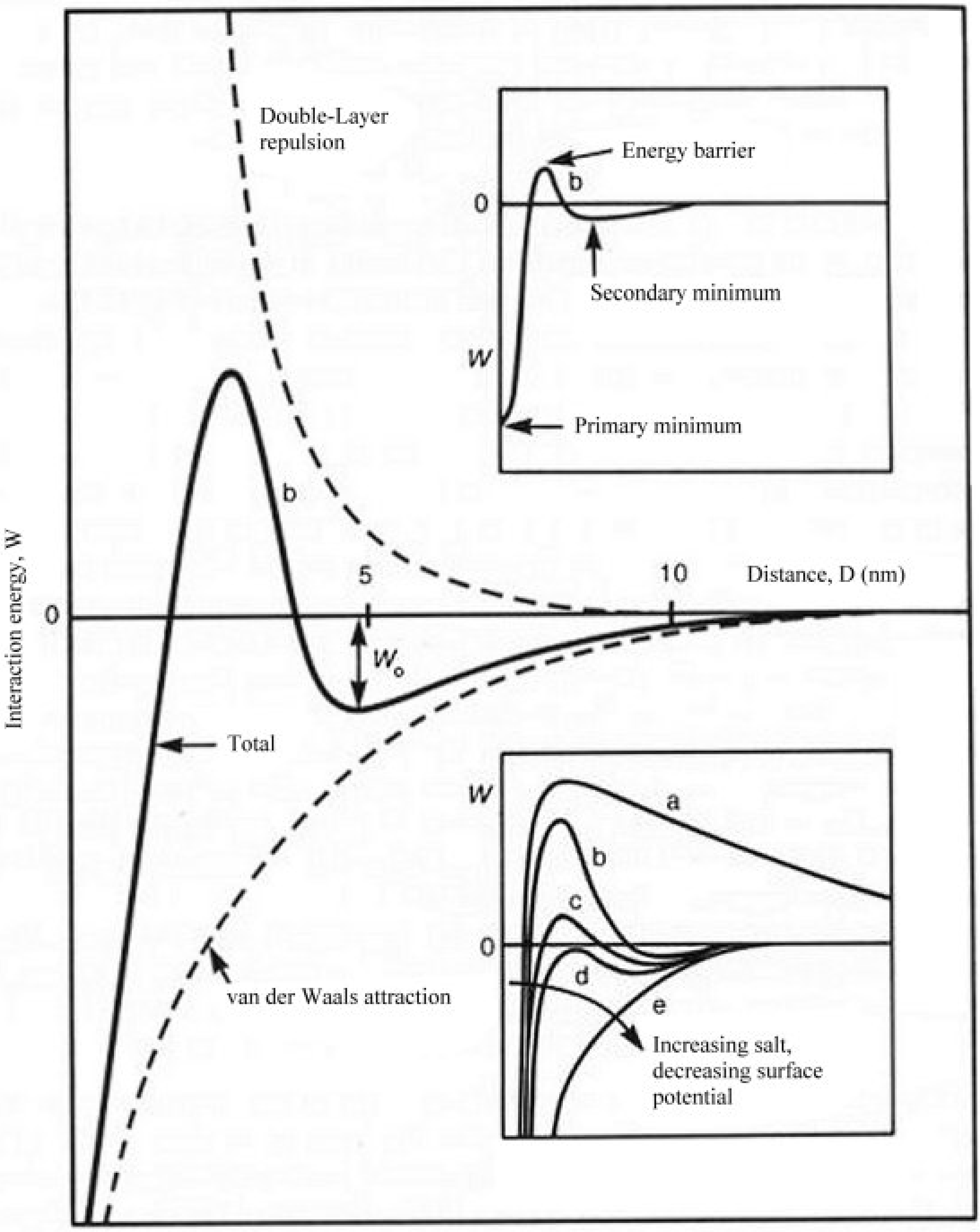

Figure 2–2: A schematic presentation of the energy versus interdistance between particles influenced by DLVO interactions. As one can see on the small scheme in the lower right corner, the potential are changing when the salt consentration are increasing. a) Surfaces are repelling eachother strongly, and small colloidal particles remain stable. b) The surfaces may stay in a stable equilibrium at the secondary minimum, but are still able to move around because of kinetic energy. c) The particles are stable in the second minimum, and are coagulating slowly. d) This is called the critical coagulation consentration. The particles may stay in the second minimum or adhere. e) All the particles are falling into the primary minimum rapidly.

trolytes and for different bulk consentrations . From the calculated values one can see that the

Table 2–2: The Debye length [nm][a]

Counterion cons. [M]	Valence 1 Na^+	Valence 2 Ni^{2+}	Valence 3 Fe^{3+}
Pure water	961	961	961
1E-5	96,1	55,7	39.2
1E-4	30,4	17,6	12.4
1E-3	9,61	5,57	3.92
1E-2	3,04	1,76	1,24
1E-1	0,961	0,557	0,392

a. The permeability for the solvent, in his case water, is 80,100 according to *Handbook of Chemistry and Physics*, 77. edition

Debye length is varying dramaticly from pure water to a high consentration of salt. For instance does an addition of 1E-1 M of sodium chloride create a decrease in the Debye length of a factor 1000. A three valence salt, as iron(III) chloride compared with a salt of valence one does also make a decrease of the length by a factor of approx. 2.5.

Though the DLVO theory gives very precise descriptions of the forces in a system of platelets, there still exists limits. The theory seems to fit well for interparticle distances above ten times the molecular size of the solvent, which is about 3nm for water. This was proved by Israelachvilis and McGuigganen (1988) [5] . Below this limit the theory does not satisfy experimental data, and we have to look for other forces and interactions like hydratisation energy, structural forces, solvation forces etc. These different effects are well described in an article by Roger G. Horn (1990) [6] .

2.2.4 Flocculation and volume of sediments

Flocculation is an effect observed in clay suspension when salt is added, and are thoroughly described in H. van Olphen [11] . I will therefore give a brief summary. Flocculation is a common term for the state of the clay when the clay platelets connects to eachother with an edge-to-edge (EE) or edge-to-face (EF) connection.which are shown in Figur 2–3. The flocculation can be observed in a clay suspension by a microscope.

The degree of flocculation has importance for the sedimentation of the clay. A flocculated suspension will have more voluminous sediments then of a stable suspension when the two suspensions are of the same consentration. This may seem paradoxical since a stable suspension consisting of repelling platelets most likly would sediment with a larger interdistance than sediments of flocs. The reason is that the particles in the stable suspension can roll and slide past eachother because of the repulsion and therefore reach the lowest energi level in the bottom of a vessel. In the flocculated suspension however the voluminous flocs pile up in the bottom of the vessel with plenty of free space between the agglomerates. The floccolated sediments can be compared with a card house. An important assumption is that the flocs are not so big that the gravity force breaks the sediment structure down.

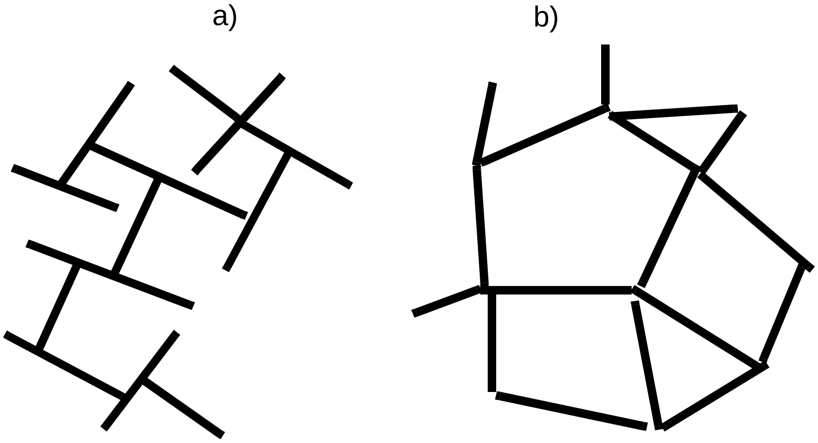

Figure 2–3: a) The clay are edge-to-face flocculated (EF) and b) the clay are edge-to-edge flocculated(EE)

The degree of flocculation are dued to the consentration of salt in the suspension, and an increase of salt in the suspension will lead to a more voluminous sedimentation. Figur 2–4 shows how the sediments are changing through increasing salt consentration in the clay sodium montmorillonite.

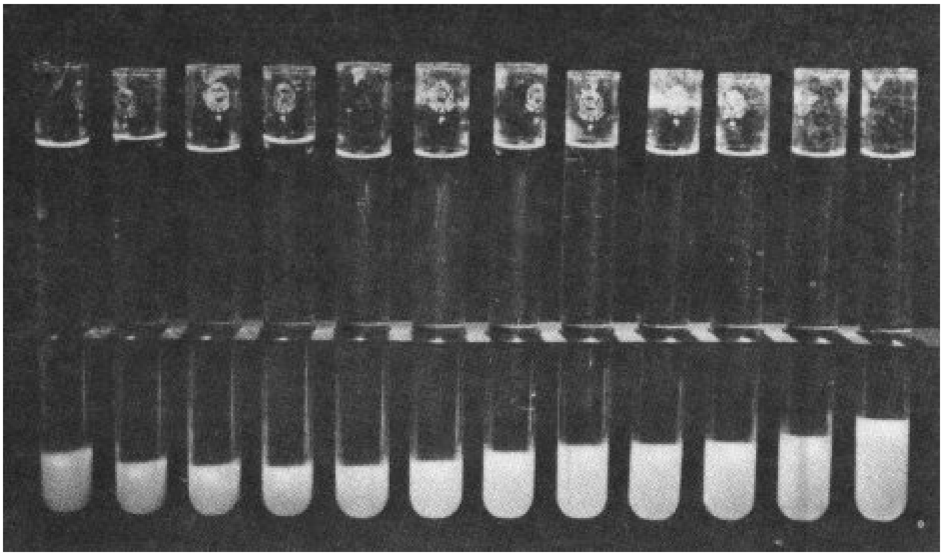

Figure 2–4: Example of sediments in a montmorillonite suspension with increasing salt content to the right.

2.3 Polarization

We know today that light has a dual nature. Einstein stated that light had a particle nature since it was possible to see a photovoltic effect, which means that light are able to release electrones from a cathode. A conditions must however exist; the frequency of the light has to exceed a lower limit. A traditional way of looking at the phenomenon of light however, is a wave model. This is regarded to the fact that interference and other similar observations was discovered early.

When dealing with the polarization effect, it is necessary to look at light as electro-magnetic waves. Through *Maxwell's equations* one can derive that both the electric field and the magnetic field is perpendicular to the direction of propagation. Since both the fields are vectors there is possible to split the ray of light into two independent components with mutual perpendicular electrical fields. These two rays are represented as

$$\vec{E}_x = E_{0x}\sin(\omega t + \varphi_x)\vec{i} \qquad [2.2]$$

and

$$\vec{E}_y = E_{0y}\sin(\omega t + \varphi_y)\vec{j} \qquad [2.3]$$

In white light these two components are equal represented and unfavourable. If now a substance supresses one of the direction one can detect that by a cross polarizator. The polarizator is an instrument allowing just one direction of the light to go through at a time.

2.3.1 Namtic phase system - liquid crystals

Normally, we consider matter to have three distinct states, represented as solid, liquid, and gas. However, there are states of matter which do not meet the necessary requirements of any of these three categories. For example, a substances such as ketchup is somewhere between a liquid and a solid.

Liquid crystals are also not quite a liquid and not quite a solid. Physically, they are observed to flow like liquids, but they have some properties of crystalline solids. Liquid crystals can be considered to be crystals which have lost some or all of their positional order, while maintaining full orientational order. An example is a large number of toothpicks put into a rectangular box and shaken. When you open the box, the toothpicks will be facing in about the same direction, but will have no definite spatial organization. They are free to move, but like to line up in about the same direction. This is a primitive model for *nematic* liquid crystals.

Nematic liquid crystals are polarizable rod-like organic molecules on the order of 20 Å in length. Because of their tendency to organize themselves in a parallel fashion, they demonstrate interesting and useful optical properties. Figure 2–5 is an example of the alignment of a thin nematic film. Because of these optical properties liquid crystals are used in display technology. The small wrist watches are one example.

The liquid crystalline phases and their thermostability was first discussed by L.Onsager [1] , and is related to a gain of translation entropy overruling the loss of entropy caused by

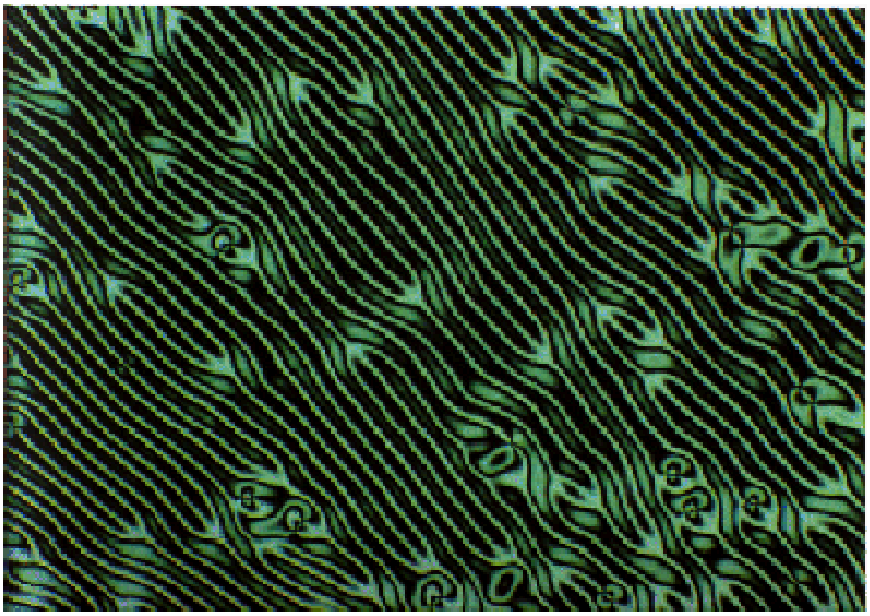

Figure 2–5: The periodic stripe structure is a spectacular consequence of the confined nature of the film. It is a result of the competition between elastic inner forces and surface anchoring forces. The surface anchoring forces want to align the liquid crystals parallel to the surface while the elatic forces work against distortions of the director field of the liquid crystal. The lowest energy state is surprisingly achived by periodical director deformations.

orientation of the crystal paricles. This yield a phase where the molecules are oriented directionally without any spatial ordering. Onsager states by his theses that a similar behavior should be observed in a system of hard plate shaped particles, which already had been observed in 1938 by I. Langmuir of macroscopic phase separations in natural clay gel [12] .

2.3.2 Detection of nematic phases

The apparence of a nematic phase in a system consisting of plates has been a problem of interest since 1938. There has been several studies of possible nematic phases in clay suspensions including two interesting articles which I have based my studies on [10,13] . The detection of these phases are done by use of a cross polarization microscope, and according to Figure 2–7 we can see some typical lines and textures related to a nematic phase. It is important to note for further reading that these pictures are taken in a cross polarizer microscope and are magnifies 50X to 100X.

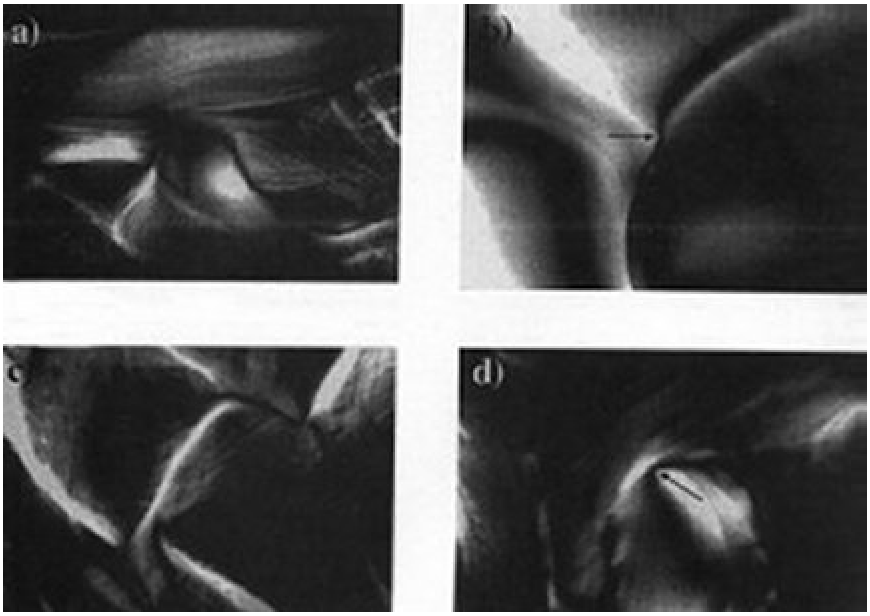

Figure 2–6: Typical structures in nematic phases in clay. Picture a) b) and c) are magnified 50X while picture d) are magnified 100X

3 Experiments

3.1 General considerations

Through my work a have prapared many samples and this has taken place for quite a long periode of time. Some conditions has, as I will point out, changed and parameters and assumptions may not stay equal all the time. I will therefore make some comments on this, even though these effects are not considered remarkebly in the conclusion.

The first aspect I will point out is the water resource used in the labaratorium. The water is firstly double destilled and is then stored in a huge plastic tank. The water is then lead into a filter (Millipore) which are ment to remove the last ion pollution. An interesting and easy parameter to check for this is the pH. The pH was found several times and gave different results. It is worth mentioning that the pH was measured by a relativly cheap pH-meter, but the meter showed stable characteristics compared to the pH 7 buffer solution that followed the equipment. The water both from the tank after the the destillation and the even purer water from the filter stayed below pH 7, and was one time measured as low as pH 6. This indicates that the water is not fully neutral, and may have an influence on the result. The conclusion to this project work includes however no accurate numbers or laws, just observations and indications. I will therefore present these facts without any further comments.

The water is normally added some ions from the water suppliance. Chlorides are added as a cleaner and to remove bacteria and flouride is put in the water because it is used as tooth health care. Both these ions were interesting to check for in the samples. The chloride was used in the ion exchange procedure to indicate when the exchange prossess had determined, which will be explained further in the following chapter. The fluoride was interesting to detect since it was suggested that the flour hectorites may release fluoride ions when dissolved in water. This is dues to the fact that laponite is releasing OH^- ions when released in neutral water, and flourhectorites are laponite with all the OH^- ions exchanged by F^- ions. A test for both chloride and fluoride was done but neither of them was detected in the water.

3.2 Preparation of clay suspensions

The clay that I used in the experiments is a hectorite called lithium fluorohectorite. This clay content lithium counterions but it was interesting to study the clay with sodium, nickel and iron. To prapare these clay suspension the first operation was to exchange the lithium ions with the desired ones. The exchange of counterions in a clay suspension are often described by the mass law [11]

$$\frac{[A]_i}{[B]_i} = \frac{K\ [A]_e}{[B]_e} \qquad [3.1]$$

where $[\ ]_i$ represent the consentration of the ions in the bulk solution and $[\ ]_e$ represent the consentration in the coating layer. A and B are the two coexisting ion species and K is the “equilibrium constant.” When there is no preference for either of the ions, K is unity. An exchange between ions of different valence will lead to a preference of the coating layer for the highest valence. I have not considered this in my experiments but it is worth mentioning.

To prepare the desired clay suspension one start with a dispersion of the clay and water in which the ions that is desired is added. The salt used was chlorides with the wanted cations. If the amount of ions added is much greater than the amount of original ions, the idea is that the the added ions will replace enough of the original counter ions. The method is based on the diploma work of Simen Lutnæs[7] . To be sure that most of the ions are exchanged, the amount of ions added was fifty times the original consentration. How the calculations of the salt needed is done is described in [7] . This clay-water-salt suspension was left for stirring and interfering for two weeks. Now the suspension was inserted into a dialyze membrane, which allowes particles of the size of the ions to pass. The clay particles however are to big and is locked up in the dialyzer. The ions not bound to the clay particles are now free to move out of the dialyzer, and by exchanging the destilled water outside ones a day, the unwanted ions will disappear. To check for this a standard silvernitrate($AgNO_3$) test for chloride ions, Cl^-, was regularly done. Some droplets of silvernitrate is initiated into the dialyze water, and if there still exists chloride ions, a white nonsoluble is easy detected. The reason is that AgCl is almost insoluble in water. When no silverchloride is observed, the clay does not contain any of the unwanted ions. Now the clay is of the kind we want and it remains to dry it and crack it to powder. After the drying the clay was rather hard and I had to it work hard to powderize it. According to former observation, this cracking is very important. If the clay is added to water when the particles are too big, they are not always totally dilluted in the water and you can see that they just float around as visuable particles.

3.3 Large scale sample of NaFHectorite

The phase structures of the small scale samples of sodium fluorohectorite discribed earlier was facinating and to study the phase transitions closer and by another scale a sample of w/w % somewhat close to the small scales where prepared. A similar test was done the summer 1999 by Chris Glass but did not succeed. The clay sol did not seem to segregate different phases except for a solid state phase on the bottom, dispite the fact that the counter ion consentration was similar to the small scale samples where 4 distinct phases were observable. Likely to believe is that the large scale system will have the same phase characteristics, but are not responding as the small scale samples because of a much longer time constant.

To investigate this an experiment with a medium scale was chosen. Instead of using a 1000 ml clay-water suspension, one tenth was used. 100 ml of water was stirred with 2,915g clay powder. Then sodium chloride (NaCl) was added in calculated portions (Table 3–1), and

Table 3–1: Large scale sample, NaFHectorite

Clay [g]	Consentration of NaCl [M]	Nematic obervations
2.915	1 10^{-4}	No
2.915	5 10^{-4}	No
2.915	1 10^{-3}	No
2.915	2 10^{-3}	Yes
2.915	3 10^{-3}	No

the sample was left nonshaking for at least 24 hours to see if different phases appeared.

The sample are shown in Figur 3–1, where one can by a careful look, see the transition line from a gel phase to a flocculated phase near the bottom of the sample.

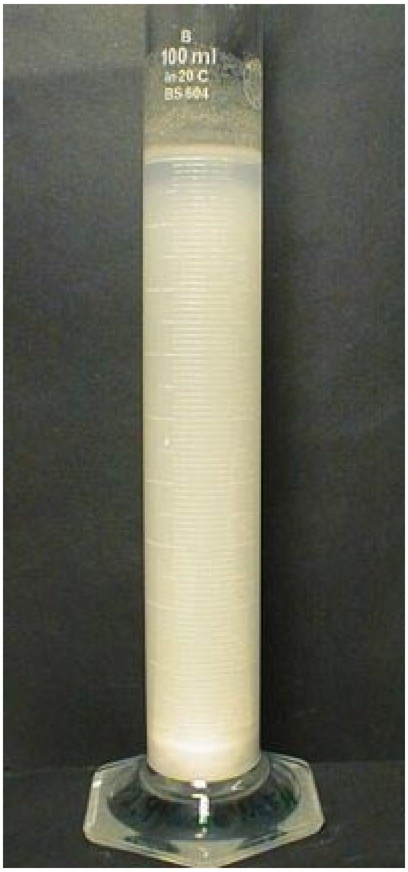

Figure 3–1: The figure shows a typical picture of the large scale sample. The samples are here containing a sodium chloride consentration of 1E-3 M

The first round of NaCl addition did not seem to create any different phases in the sample, similar to Figure 3–1. When the salt consentration reached 2 10^{-3} however it was possible to see at least three different phases, one containing some beautiful polarization textures in the upper gel phase as Figure 3–2 shows. The structures of the polarized phase of the suspension are similar to Figure 2-6 but there is still a difference. These apparent structures are by a different scale. These ones are taken by a 1:1 scale while the one shown earlier are by a 1:50 or 1:100 scale.

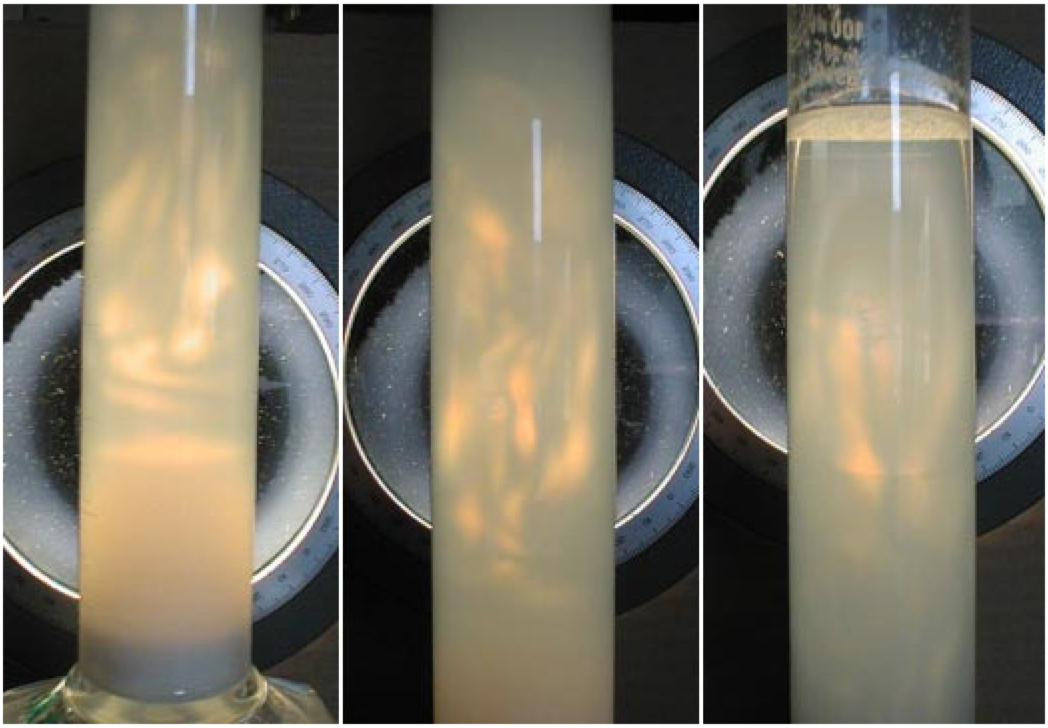

Figure 3–2: Polarizations in a large scale NaCl

3.4 Small scale samples of NaFHectorite

3.4.1 The first samples

Different phases in the same sample had been observed but a closer research of the mechanisms was interesting. The start of my work was a preparation of samples of sodium fluorohectorite with different amount of sodium chloride added. The samples were made from already prepared NaFHect, produced by former project work student Simen Lutnæs [7] . These samples were dry and compact , and had to be cracked to powder before it was added to the double destilled water in order do dissolve. The clay suspension was stirred for 24 hours before the salt sodium chloride was added in the right quantity. The samples were taken from the stirring cup and transfered to small cyvettes.

The cyvettes were sealed by some electrical paste, and were left in order to segragate into different phases. The sealing paste did not satisfy our demands and after two months one could see that small amount of water was escaped.

After one week the samples seemed to be stablized and some pictures were taken. The pictures revealed interesting lines and phase separations in the samples which are easy to see in Figur 3–3 and Figur 3–4. From the graph following in Figure 3-5 one can more clearly see

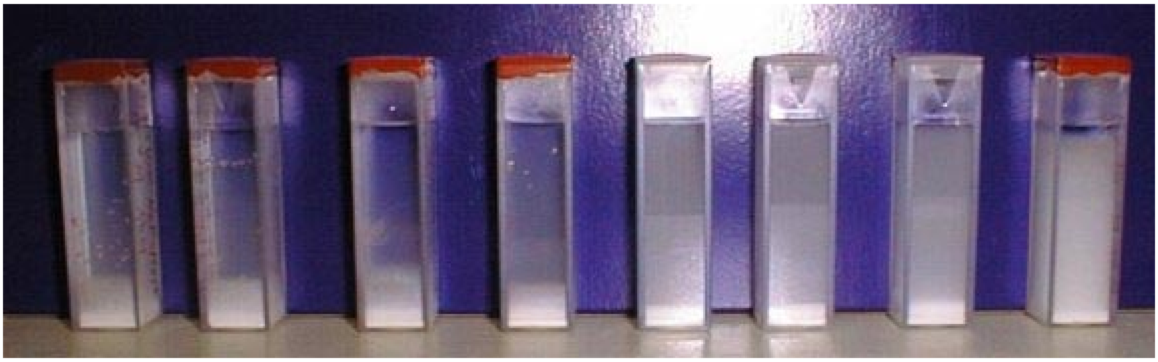

Figure 3–3: The small scaled samples of sodium fluorohectorite. From left the sodium chloride consentration are 1E-4, 5E-4, 1E-3, 3E-3, 4.5E-3, 6E-3, 8E-3 and 1E-2 M.

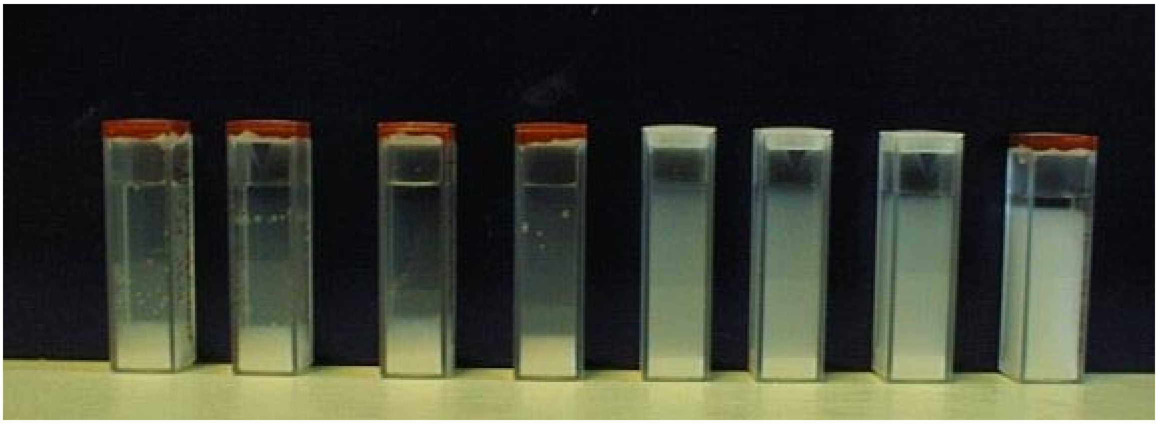

Figure 3–4: This shows the same samples as Figure 3-3, but without using flash.

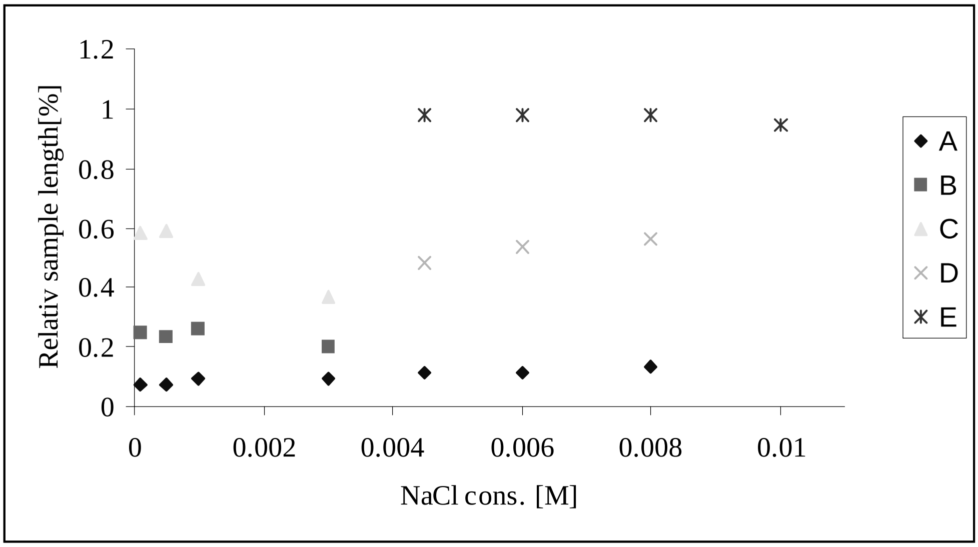

Figure 3–5: The graph shows the phase shifts for the series of samples in Figure 3-3 and 3-4.

some of the trends in the clay suspension. I have used different colours in the graph on the phases that I have considered to be of a different kind.

3.4.2 Small scale NaFHect and polarization

The small scale samples prepared in the spring 1999, presented in the previous chapter showed that the sodium fluorohectorite suspension may content at least four different phases at the same time. A question to ask is naturally what kind of phases they are, and what characterize them. A first approach to this problem is to investigate the different phases ability to polarize homogenous light propagating through the dispersion. If the phases had some nematic character as discribed in the chapter «Namtic phase system - liquid crystals» one could possibly define the phase as nematic. A problem however was our cyvettes. They were made of a polarizing material and it was impossible to decide if an apparent polarisation effect was dued to the clay suspension or the cyvettes. To avoid this problem some cyvettes where made by the glass master at the Dept. of Physics (Figur 3–6).

Figure 3–6: An example of the glass cyvettes

The clay suspension was prepared as described before containing the same amount of salt, and put into glass cyvettes and was left undisturbed for one week. The result are showed in Figur 3–7. Suprisingly the samples show different characteristics than the one prepared earlier, which by the first look would indicate that some mistake had been done one of the times.

Now it was possible to check for polarizing effects in the dispersion and Figur 3–8 to Figur 3–14 show the cross polarized samples compared with the salt content.

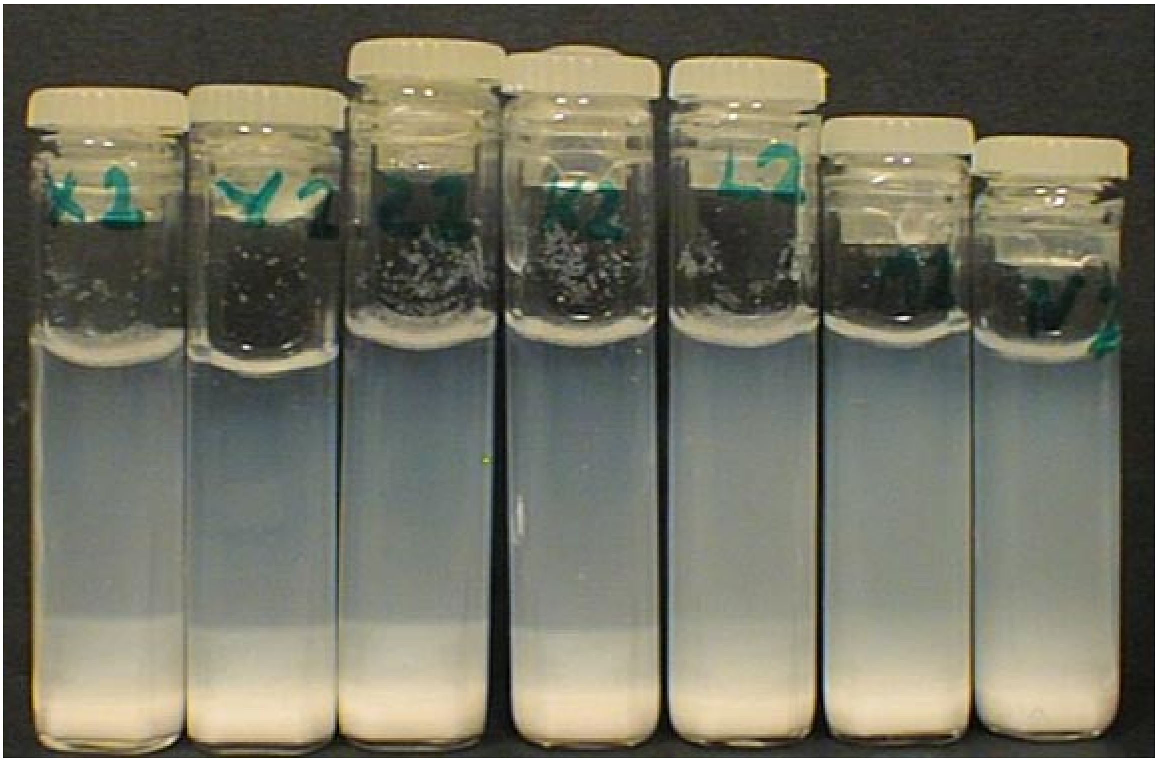

Figure 3–7: Sodium chloride hectorite with increasing salt consentration to the right. The NaCl consentration are from the left 1E-4, 5E-4, 1E-3, 2E-3, 4E-3, 6E-3 and 8E-3 M.

Figure 3–8: A cross polarized picture of two sodium fluorohectorite samples with a sodium chloride consentration of 1E-4 M.

Figure 3–9: A NaCl consentration of 5E-4 M

Figure 3–10: A NaCl consentration of 1E-3 M.

Figure 3–11: A NaCl consentration of 2E-3 M.

Figure 3–12: A NaCl consentration of 4E-3 M.

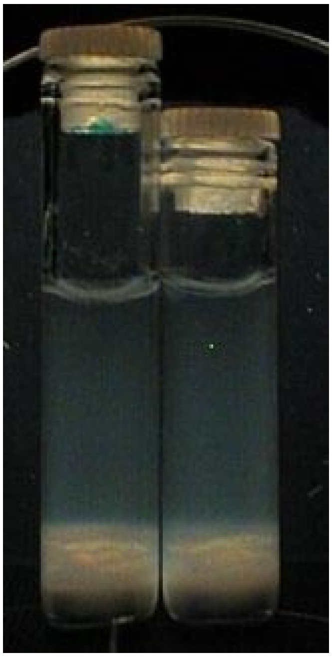

Figure 3–13: A NaCl consentration of 6E-3 M

Figure 3–14: A NaCl consentration of 8E-3 M

3.5 Nickel fluorohectorite

In the planning of my project work the aim was to registrate the different phase behaviours dued to the changing valence of iron, nickel and sodium. By considering the Debye length in Table 2–2 on page 8, one easy see that the range of the force between the clay particles are dependent on the valence. Because of a slow ion exchange and a shortage of time I did not manage to make iron fluorohectorite, but at least an interesting behaviour did occur in the nickel samples (Figur 3–15 and graphically in Figure 3-16).

Figure 3–15: The figure shows an increasing line between the two phases.

As computed earlier the Debye length are increasing by increasing consentration of ions in

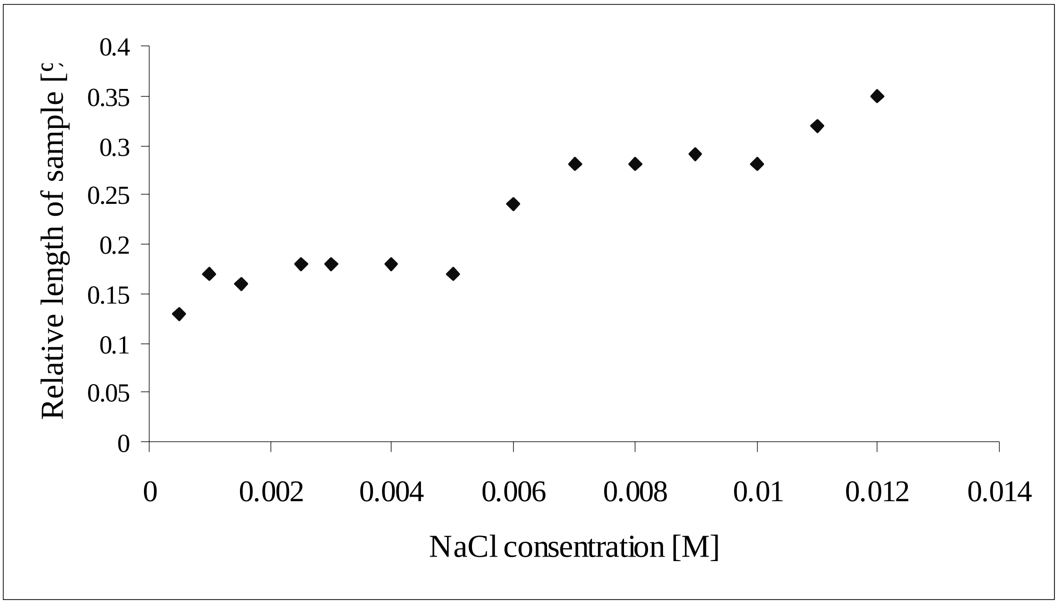

Figure 3–16: The graph shows the relative length of the sedimented phase of Figur 3–15. There is a trend that the volume of the sediments is growing when the consenration of NaCl are increasing.

the bulk dispersion and yield a shorter Debye length. The clay particles need to get closer to see eachother and in some way flocculate. The figure however indicates that the increasing amount of ions added leads to a greater distance between the particles in the flocculated phase. One can visually see that the transition line between the flocculated phase and the liquid phase is raising to the right (by increasing salt consentration).

3.6 Clay before salt and vice versa

From a previous work [7] it was made clear that the order of addition of clay powder and salt into water was rather desicive. Salt alone put into water will change the Debye length of the dispersion a lot, and when clay is added, the reaction will be different. It was interesting to check this out and therefore two suspension were prepared, one with salt added first and one with clay first. The samples were made with sodium fluorohectorite since it was the clay I have been working with mostly, and are shown in Figur 3–17. It was a surprising observation that the two samples did develop the same phase shifts and did not show different dynamic behaviour as expected. By accident I discovered that one of my fellow students Kristian Mjøen had done the same test for synthetic montmorillonite. Here the to samples differed alot. It is however a fact that the salt consentration of these samples where considerably higher (about 2E-1 M). It should be clear that the order of clay and salt are more important for high salt consentrations.

Figure 3–17: The samples did not differ in properties whether salt or clay was dilluted in water first. The salt consentration are approx. 1E-3 M in both samples.

4 Discussion

Through my work I have discovered and observed some interesting things in the clay suspensions, and it demands some deaper explanations. I will not be able to conclude on most of the observations since a much more thorough investigation are neccessary, but I will in this part try to look for some common features for the different experiments.

4.1 Sodium fluorohectorite

Different experiments have been done with sodium fluorohectorite and interesting observation are achieved. First of all the first observation I did in the lab was the phase separation of the small scale samples shown in Figur 3–3 and Figure 3–4 on page 17. The pictures indicates quite clear that some phases are disappearing and some new phases are appearing. An interesting observation is that something is happening when the sodium chloride consentration are passing about 2-5E-3 M as one can see in Figur 4–1. The different phases are indicated by letters, and if one try to trace them it is most likely by a visual consideration that the phase *A* is the same as *a*, *B* the same as *b* etc. The question who raises are however if these phases really are the same ones. It is possible that there is a sudden phase shift in the clay suspension when the salt consentration passes about 2-5E-3. If we are looking back to Figur 3–4 it is easy to registrate that phase *c* is actually schrinking when the sodium chloride consentration are increasing. It is therefore not probable that the *C* phase is the same as phase *c* since *C* is much wider. One can assume that both *B* and *C* are phases with different properties as *b* and *c*. Both *a* and *A* are sediments, and of the approx. same size for all the consentrations, the properties may however vary with this phase as well («Flocculation and volume of sediments»).

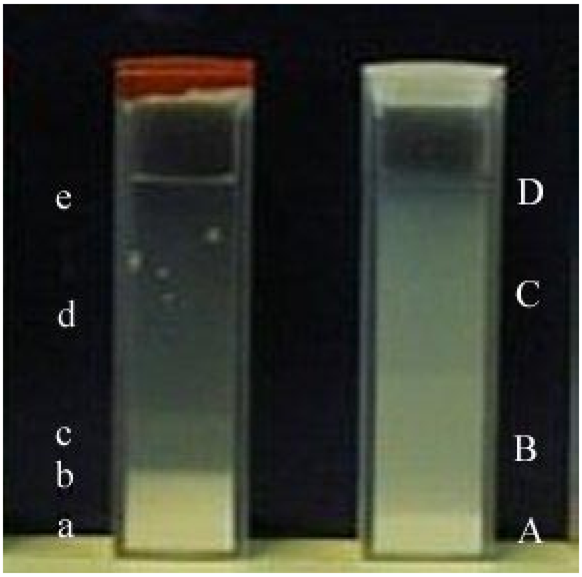

Figure 4–1: The transition between 3E-3 M and 6E-3 M sodium chloride in the clay

The polarized pictures of the other sodium fluorohectorite samples shows as mentioned some different behavior. The idea with these samples was to check for polarizing phases as for instances nematic structures. The samples are shown in Figur 4–2 as well, and one can see

Figure 4–2: The small scale sodium fluorohectorite samples lined up with increasing sodium chloride consentration. A)1E-4 M NaCl B)5E-4 M NaCl C)1E-3 M NaCl D)2E-3 M NaCl E)4E-3 M NaCl F)6E-3 M NaCl G)8E-3 M NaCl.

that the behaviour are the same in the four leftmost samples, containg only three phases. This is not consistent with the first samples in the first series of samples although they have the same NaCl consentration. This observation are really hard to explain. The first option is that the two series of samples are not containing the same amount of one ingridience. My first guess was that the clay powder in the second series was including some NaCl so that the ion-consentration actually was higher than I had calculated. After some testing for Cl^- ions of the clay powder I had used, this reason was rejected.

A most interesting observation when focusing on the great differences between the two series are one obvious similarity. The first series shows a quick change in the properties about 2-5E-3 M of NaCl. By studying Figur 4–2 one can see that something is happening between sample D and E, which hold a consentration of 2E-3 M and 4E-3 M, exactly the same interval as for the first samples. This may indicate that although the the samples show great differences in properties they still shear one important feature.

The same effect is seen for the large scale sample, where the region of polarized clay just are observed with a NaCl consentration of 2E-3 M. Neither a higher nor a lower consentration gave the same beautiful polarized structures. All these observations together makes it reasonable to believe that something is happening to the clay suspension with a sodium chloride consetration of about 2-5E-3 M.

4.1.1 Sodium fluorohectorite and polarization

As one can see both from the large scale sample and the small scale samples there are region where light are polarized. The polarized region for the large scale sample occur however only for one consentration, while for the small scale samples there is a polarized phase at the bottom of all the different consentrations.

To have a look at the large scale sample first, one can see some really nice structures in the middle phase which are similar to the the picture in Figure 2–5 . The light lines and regions are similar, and one can easy conclude that the polarized region of Figure 3–2 are a nematic phase. There is some more important information though. The scaling of the picture from the large scale sample is a normal 1:1. The picture of the typical nematic fingerprints are at a 1:50 and 1:100 scaling. The order of scaling makes the comparation somewhat more complicated. It is clear that alignments of clay aggregates over a distance of 1mm does not have to be caused by the same forces as an alignment over a distance of 10µm.

The small scale samples are also showing polarizing properties (Figur 3–8 to Figur 3–14). The polarized phases states the same as a view by eyes, namely that the samples are equal untill the NaCl consentration reaches about 2E-3 M, In Figur 4–3 one can see that the transition line between the region influenced by cross polarized light and the unpolarized phase is very sharp. By increasing the NaCl consentration to 6E-3 M the transition line are broader and the polarizing region are faded out. From the two samples to the right it actually looks like two phases are coexisting and that one of them consist of clay aggregates that polarize the light in a way that makes it visuable for the eye, while the other phase also undoubtably polarize the ligth, but there is not possible for the bare eye to detect any structure. A cross polarizing microscope is necessary to decide wether there are structure in this region or not.

Figure 4–3: Small scale sodium fluorohectorite samples that are crosspolarized. The two samples most left contain a NaCl consentration of 2E-3 M while the two at the rigth 6E-3.

4.2 Sedimentation in nickel fluorohectorite

The sedimentations of nickel fluorohectorite (Figure 3–15) seems to show an obvious trend. First of all the samples contains only two apparent phases. One is a liquid phase without any polarizing effects and the other is a solid state of sediments. This makes it easier to study what is going on when we change the ion consentration. Secondly the level of sediments most clearly increase when increasing the $NiCl_2$ consentration. As described earlier in «Flocculation and volume of sediments» this increase in sediments of montmorillonite is related to the flocculation of the particles in the suspension. This may also be the reason for the similar behaviour in the NiFHectorite suspension. An increasing salt consentration implies a shorter range of the screening length, or Debye length, which allows the particles to get closer to eachother. When they are getting close enough occationally one particles may stick to another because it is “caught” in the potential minimum from the other. The way the particles are connecting to eachother decides how voluminous they are in a sediment. If two platelets are piling up like in Figur 4–4 A) in bigger aggregates, the sediments will be much less voluminous as if they first are flocculating like Figur 4–4 B) and then falls to the bottom and create sediments.

Figure 4–4: Clay aggregates can create sediments in different ways. A) The clay platelets starts piling up like a pile of cards and than make a rather compact sediment. B) The platelets may instead couple to eachother in a face-to-edge or edge-to-edge manner greating a sediment with free space in between.

4.3 Phases and phase transitions

Clay systems are showing a richdom of different phase constellations, and the complexity of this system makes it difficult to come up with a general theory. Some computer simulations have been done [13,14] , but the results show deviation from experimental values. To create a computable model of the system one has to take into account some assumptions, which removes the model too far from reality. A quantitative analysis of the observations done may however give indication of how the clay system are acting.

The behaviour of the nickel fluorohectorite samples discussed in the previous chapter may explain how liquid and gel phases are acting as well. If a phase consists of flocculated aggregates of particles in some sort of gel phase, one can imaging that an addition of more counterions, which implies that the Debye length decreases, can lead to a more voluminous phase. This will cause a broadening of the region where this phase exists. This expansion are for instance seen in the small scale samples of sodium fluorohectorite in Figure 3–4 , where a new phase are growing forth in the three rightmost samples.

This only explains some few of the observations, and it is also obvious that phases are disappearing when the salt consentration are increasing. Sudden phase shifts as observed can be explained in different ways but the following explanation must be considered just as suggestions. For instance is the clay platelets of finite size, and the edges are charged as the plain surface. When the Debye length is decreasing, one can imagine that at a certain level the platelets start to connect to eachother in a face-to-edge manner. One platelet can get close enough to another to get caught in the potential minimum. Several particles together becomes a new particle with different properties, and will seperate from small platelets and we have two phases.

It is possible to see different combination where particles of various size connect and reconnect in different ways dependent of the counterion consentration, and this complex system of interaction between the clay particles and the ions in the dispersion creates all together the phase shifting system in the clay suspension.

5 Conclusions

This report of my project work does not give any precise results, and it is therefore difficult to give absolute facts and conclusions. The most important discovery I have done is that scientific work demands alot of prestudies and thorough investigations to achieve new information. The results and data that I have collected are however of some importance for further studies, and I will focus on that through this chapter.

A major result from my work is the behaviour of the 3w/w % sodium fluorohectorite samples. It is obvious that something radically, for instance a phase shift, is apparent about a sodium chloride consentration of 2 -5E-3 M. This is observed in both the series of small scale samples, and the large scale sample. To consentrate on the large scale sample first, the polarized suspension indicates that the particles are in some way lined up in a certain way. This may be dued to the excistance of a nematic phase in the sample, but since I was not able to take pictures with a microscope, it is still unknown wether this sample show the same properties at a 1:100 scale as the pictures presented in [10] . A continuation of this work will be to study this region of the sample through a crosspolarize microscope.

Another thing that I experienced was that the dynamic periode of the large scale sample, which mean the time before all the phases are at equillibrium, is much longer than I had expected. The samples were left in piece only for about two weeks. A necessary time periode is at least two months, which means that I was not able to see the final distribution of the phases in my work. An interesting project is to study this segragation with this fact in mind. To speed up the prossess a sentrifuge may be used. Since the system are very slow the dynamics of the system are possible to study more thorough. One can imagine that a closer study of how the phases separate will give information of the size distribution of the clay particles and how they interact.

The DLVO theory explains the forces between particles with an interdistance above ten times the dimensions of the solvent. If the particles are getting closer many other effects are need to be taken into account and the system becomes much more complex. Despite this complexity one can based on observation give qualitative explanations. The nickel fluorohectorite samples show a relativly simple behaviour when the nickel chloride consentration increases. This is similar to observations in montmorillonite and it is likely to believe that it is caused by an increasing degree of flocculated particles. If the platelets are connecting in a more and more voluminous way because of the salt consentration the sediment will need more space, and the observation will be a raising level of the sediment. A question one can ask is what will happen when the nickel chloride consentration are increased even more? Maybe will the sediment phase to some extend devide into different phases where some of the aggregated particles are still sedimenting while smaller ones will create a gel or liquid phase. This are just thoughts and suggestions, but the NiFHect samples with this consentrations have the advantage that they contain only two phases, which makes them easy to study.

Appendix A The samples

To be able to reproduce the results and samples for a later occation I will in this appendix present all the clay and salt consentrations which have been produced.

The first small scale series.

The samples where prepared as mentioned in the report with clay dispersed before the salt was added.

Table 5–1: Small scale sample. First series.

Sample no.[a]	Clay cons [w/w%]	Salt cons.[M]	Comments
1	2.91	1E-4	
2	2.91	5E-4	
3	2.91	1E-3	
4	2.91	3E-3	
5	2.93	4.5E-3	made later
6	2.93	6E-3	made later
7	2.93	8E-3	made later
8	2.91	1E-2	

a. The number is referring to the order in Figure 3-3.

The second small scale series.

Table 5–2: Small scale sample. Second series

Sample no.[a]	Clay cons [w/w%]	Salt cons.[M]
1	3.00	1E-4
2	3.00	5E-4
3	3.00	1E-3
4	3.00	2E-3
5	3.00	4E-3
6	3.00	6E-3
7	3.00	8E-3

[a] The number is referring to the order in Figure 3-7.

Large scale sample

The large scale sample was prepared in one vessel, so it is not really different sample but the same sample with salt added. Pictures were taken between every consentration increase.

Table 5–3: Large scale sample

Clay cons [w/w%]	Salt cons.[M]	Remarks
2.92	1E-4	
2.92	5E-4	
2.92	1E-3	
2.92	2E-3	Polarized
2.92	3E-3	

Nickel fluorohectorite samples

This samples where prepared as the small scale sodium fluorohectorite samples, but in lack of clay powder, the data for these samples are very uncertain. The Figure 3-17 are showing the samples. It is worth remarking that the first four samples were prepared first.

Table 5–4: The NiFHect. samples

Sample no.[a]	**Clay cons [w/w%]**	**Salt cons.[M]**
1	2.49	5E-4
2	2.49	1E-3
3	2.49	2.5E-3
4	2.49	5E-3
5	2.49	3E-3
6	2.49	4E-3
7	2.49	5E-3
8	2.49	6E-3
9	2.49	7E-3
10	2.49	8E-3
11	2.49	9E-3
12	2.49	1E-2
13	2.49	1.1E-2
14	2.49	1.2E-2

[a] The number is referring to the order in Figure 3-17.

Bibliography

[1] Lars Onsager *The Effect of Shape on the Interaction of Colloidal Particles* Ann. N.Y. Acad. Sci., 51, [31], 1949, 627-659.

[2] Jacob Israelachvili *Intermolecular & Surface Forces* second edition 1991 p214

[3] Simen Lutnæs *Forberedelser til akustiske målinger på leire* 1998 p12

[4] Preben C. Mørk *Overflate og Kolloidkjemi - Grunnleggende prinsipper og teorier.* Institutt for Kjemi, 5.utgave 1997.

[5] J. N. Israelachvili & P. M. McGuiggan *Forces between surfaces in liquids*. Science 241, 1988, 795-800.

[6] Roger G. Horn *Surface Force and Their Action in Ceramic Materials*. Journal of Ceramical Scociety, 73, [5] 1990, 1117-1135.

[7] Simen Lutnæs *Experimental studies of water intercalation in layered silicate system* Diploma thesis, Feb. 15, 1999.

[8] P.D. Kaviratna et al. *Dielectric Properties of Smectic Clay.* J. Phys. Chem. Solids, Vol 57, No. 12, 1990, 1897-1906.

[9] Bruce Velde *Origin and Mineralogy of Clays - Clays and the Environment*, 1995.

[10] J-C.P.Gabriel et al. *Observation of Nematic Liquid-Crystal Textures in Aqueous Gels of Smectit*e Clays J. Phys. Chem., 100, 1996, p11139-11143.

[11] H. van Olphen *Clay Colloid Chemistry* National Academy of Sciences, Second Edition. 1991.

[12] Irving Langmuir The Role of Repulsive Forces in the Formation of Tactoids, Thixotropic Gels, Protein Crystals and Coacervates J. Chem. Phys. Vol 6, 1938, 873-896

[13] F.M. van der Kooij and H.N.W. Lekkerkerker Formation of Nematic Crystals in Suspensions of Hard Colloidal Platelets J. Phys. Chem., 102, 1998, p7829-7832.

[14] Martin A. Bates and Daan Frenkel *Nematic-isotropic transition in polydisperse systems of infinitely thin hard platelets* J. Phys. Chem. Vol 110, No 13, 1999