

Preparation for
“A Microscope Study of Nano Silicates”

Svein Åsmund Slungård
Department of Physics, NTNU, N-7491 Trondheim Norway

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Abstract

This project was an experimental study of electrorheological (ER) effect in clays dispersed in paraffin. The paraffin is found to be a suitable solvent in most cases. When the clay laponite RD is used, wide visible chains are observed when applying an external electrical field over the cell. When trying with paraffin and laponite RD in a rheometer, the ER effect is undetectable due to very fast sedimentation. A lipophilic laponite clay, Alkyl quaternary ammonium smectite (AQAS), was tested in the same way as with laponite RD. The chains are in this case much more narrow, and slightly dimmer, indicating a weaker ER performance. The AQAS yields a strong ER effect in the rheometer, with a stronger effect using paraffin as solvent than with the sample dispersed in silicone oil. The sedimentation is considerable less in AQAS than in the laponite RD. Attempts of taking pictures of the chains with an atomic force microscope were also performed. No pictures with evident chains were achieved, but the method proved promising.

Laponite RD was then treated with a surfactant compound, CTAB, to make the clay lipophilic. The CTAB treated clay gives a chain formation, not unlike the chains with the untreated laponite RD. The sedimentation is not very different from the untreated clay, not a very good sign compared to the low sedimentation in the supposable similar AQAS clay. The surface modification experiment can only be said to be partly successful though this experiment is still in its initial stage.

Chapter 1

Preface

This report is the documentation of the project part of the bipartite course in the ninth semester of the Master degree in Physics (Sivilingeniør) at the Norwegian University of Science and Technology (NTNU). The work is done at the Complex Materials Group at Department of Physics.

I would like to acknowledge my supervisor Professor Jon Otto Fossum for valuable instructions, Post.doc. Ahmed Gmira for good advices and help with the AFM, and finally my collaborator Børge Aune Schjelderupsen for good teamwork.

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Svein Åsmund Slungård

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Chapter 2

Introduction

The object of this project was to investigate the electrorheological (ER) effect in suspensions of clay and paraffin. Such ER fluids can switch from liquid to solid state within milliseconds when an electrical field is applied, due to a major change in the viscosity. This ability to easily control the phase of a suspension is of great interest in various industries like robotics, automotive and military industry[1].

In electrorheology, the dispersed particles tends to form chain structures when the electric field is applied, and the visual observation of these chains was the main task for the project. The paraffin was melted to be able to perform the experiments, and when the paraffin solidified, the field could be turned off, and the sample taken under observation with an optical microscope. This was done with different kinds of clays. First the Laponite RD, a synthetic silicate, which works as a reference for the other clays, was investigated. The second kind of clay is the Alkyl quaternary ammonium smectite (AQAS), a surface modified laponite clay which is lipophilic and thus disperses much easier in paraffin than laponite RD. Finally, the dangerous border to chemistry was crossed when trying to treat the laponite RD with CTAB, a cationic surfactant. If successfully, the clay should act not very different from the AQAS, due to the similar structure.

Paraffin is a rarely used compound in such kind of experiments, and part of the project was to investigate the behavior and suitability of paraffin as a solvent for clays, and for ER performance. As a part of this, samples with paraffin were investigated with a rheometer.

The work has given good insight into practical lab work through designing the cell and experimental setup, and through the sample preparations and analysis. It has also shown that experimental work in physics often proves to be very time-consuming.

The experiments with paraffin in the rheometer and the surface modification

with CTAB were performed in collaboration with Børge Aune Schjelderupsen. This project is meant to be a preparation for my master thesis during spring 2007, so unfinished experiments presented in this report are supposed to be continued in upcoming work.

Part I

Theory

Chapter 3

Electrorheology

Materials that can undergo a phase-transition from liquid to solid state under the application of an external electric field are termed *electrorheological fluids* and were first described by W. M. Winslow[2] in 1949. The electrorheological fluid consists of finite-conductive polarizable particles in an insulating fluid, often an oil. The shear stress and viscosity of the fluid increases tremendously, often with several orders of magnitude, when field strengths of the order of $1 \frac{\text{kV}}{\text{mm}}$ is applied. The solidification can occur within milliseconds when working with large fields. This behavior comes from a structural change of the suspended particles. When the field is applied, field-induced dipoles attract each other and tends to form chain structures in the direction of the field, see Figure 3.1.

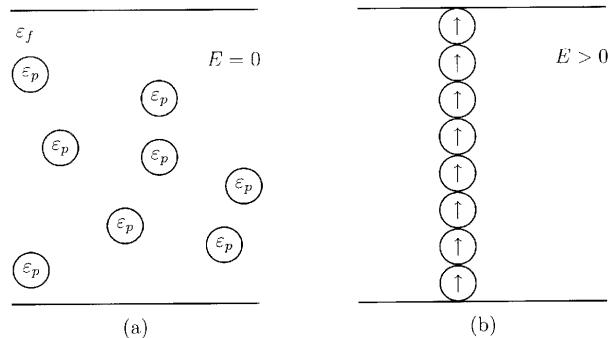


Figure 3.1: Electrorheological effect. a) Without an electric field, the particles, dispersed in a liquid, with dielectric constant ϵ_p are randomly oriented. b) When the electric field is applied, the particles are polarized and orients in the direction of the field, forming chains and aggregates[3].

The chain structures restrains the fluid flow and therefore increases the viscos-

ity and the shear stress. This effect is entirely reversible and the ER effect will disappear and the fluid recover its original state within the same time-scale as it occurred when the electrical field is removed. This fast, strong and reversible change in the rheological properties, provides a wide range of possible applications such as dampers, clutches, brakes, valves and actuators. Despite of this huge potential, few ER devices are available. This has to do with the lack of effective fluids[1, 4, 5, 6, 7].

To achieve satisfying ER performance for an application, the fluids should fulfil several requirements where the most important are high dynamic yield stress, large increase in viscosity, fast response time, low current density through the fluid, stability against sedimentation, chemical degradation and irreversible flocculation. In addition, these fluids must also be able to operate over large temperature ranges. The complexity of the behavior of the fluid is also a problem in the design of ER devices. It is dependent of variables such as electrical field strength and frequency, deformation history, temperature and composition. In addition the solution often includes additives like surfactants and activators to improve the ER effect, complicating the situation even further[6, 7].

3.1 The Polarization Model

Electrostatic polarization models can describe many experimentally observed features of the ER fluids, such as the formation of aggregates and field strength and concentration dependence of formation properties. The agreements between observations and models suggest that polarization interaction between particles is the origin of the ER effect[7].

The polarization can be described using a simplified model based on identical spherical dielectric particles dispersed in an insulating fluid. Responses are assumed to be linear. Under the application of an electric field, each particle in the fluid is polarized, see Figure 3.1. The induced dipole moment is given by

$$\mathbf{p} = \frac{\epsilon_p - \epsilon_f}{\epsilon_p + 2\epsilon_f} \epsilon_f a^3 \mathbf{E}_{\text{loc}}, \quad (3.1)$$

where a is the radius of the spherical particle. ϵ_p and ϵ_f are the dielectric constant for the particles and fluid, and \mathbf{E}_{loc} is the local electrical field. The polarization is caused by a mismatch in the dielectric constants[3]. Equation (3.1) indicates that particles with large ϵ_p provides the strongest ER effect. This is not always the case, and demonstrates that the polarization model approach not always is sufficient. The model can not explain phenomena like the dependence of the electrical field frequency or the dependence of particle conductivity. The conductivity can be included in the polarization model by replacing ϵ with the complex permittivity. Such a model can describe the observed physics better than the simple polarization model, but the drawback of both methods are the

lack of prediction for dynamic systems, i.e. they only apply after the micro structure has fully formed[8].

There exist more advanced and powerful models which can describe the observed physics better, e.g. a model by Khusid and Acrivos[9], but these are beyond the scope of this project.

3.2 Bingham Fluids

Bingham-fluids are non-newtonian fluids which are characterized by a yield stress. As opposed to newtonian fluids they can transmit a velocity gradient without a shear stress. To make a Bingham-fluid flow, one must have a shear stress larger than the yield stress, which means that for shear stresses below this limit, the fluid will behave like a solid, and above the limit, as a fluid[10]. The electrorheological shear-response is commonly described with the Bingham model. The shear-stress τ is described as

$$\tau(\dot{\gamma}, E_0) = \tau_0(E_0) + \eta_{pl}\dot{\gamma}, \quad (3.2)$$

for $\tau > \tau_0$. $\dot{\gamma} = 0$ for $\tau < \tau_0$. Here is E_0 the applied electrical field, $\dot{\gamma}$ the shear rate, τ_0 the dynamic yield stress and η_{pl} the plastic viscosity[7]. The yield stress τ_0 is found theoretically and experimentally to follow the relation

$$\tau_0(E_0) \propto \Phi^\Delta E_0^\alpha, \quad (3.3)$$

where Φ is the volume fraction of particles. The polarization model predicts that $\Delta = 1$ and $\alpha = 2$ [8]. For low and moderate field strengths it is observed $\alpha \approx 2$. For high fields, the magnitude of α decreases somewhat[7].

Chapter 4

Surface Treatment

4.1 Surfactant

Surfactants are usually organic amphiphilic molecules. The term amphiphilic means that the molecule has one hydrophilic part, usually called the “head”, and one hydrophobic part, often a long hydrocarbon chain, usually called the “tail”. This amphiphilic nature makes the molecule solvable in both water and organic solutions. The CTAB molecule shown in Figure 6.7 in chapter 6, shows a typically example of such an amphiphilic surfactant, with the characteristic “head & tail” design. When present in a solution over a certain concentration, the surfactant molecules aspire to make micelles. A micelle is an aggregate of surfactant molecules, where the molecules tends to minimize the contact between water and the hydrophobic part by encircling the hydrophobic tails with the heads. If the surfactant is solved in organic material, in this case oil or paraffin, the hydrophilic parts will be in the core, and the micelle is said to be reverse, shown in Figure 4.1[11].

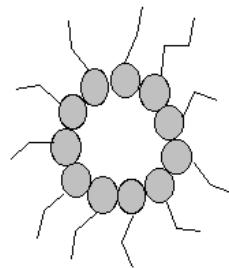


Figure 4.1: Schematic of a reverse micelle, showing the hydrocarbon chains creating a protecting shell around the hydrophilic parts.

4.2 Quaternary Ammonium Cation

The quaternary ammonium (QA) cation is a positively charged ion of the structure NR_4^+ , where the Rs are alkyl groups. These alkyl groups can be different in size and even connected. Unlike normal ammonium ions, the QA is permanently charged, at any pH. These ions, or actually salts of this ion, can be used as surfactants[12], in our case, to modify the surface of clays. The CTAB (see section 6.3 and 4.3) is such a QA salt. The already modified clay, Alkyl quaternary ammonium smectite,(see section 6.1.2) is as its name describes, modified with QA, to become lipophilic¹.

4.3 Ionic Exchange

Ion exchange is a reversible process where dissolved ions are taken up by a solid, replacing ions already attached to the solid. The amount of charge does not change neither in the solution nor on the solid in this process[13]. The property of adsorbing and absorbing ions in a solution is called *cationic exchange capacity*, CEC. This is a measure of the total number of charged ions which can be fixed onto the surfaces of clays, more specific the number of moles of ionic charge fixed on 100 g dry clay. The unit of the CEC is $\frac{\text{milli-equivalents}}{100 \text{ g}}$ or $\frac{\text{meq}}{100 \text{ g}}$. If ions or charged molecules in a solution can be attracted to a clay surface there will be a selection between the species available. The more there exist of an charged species in the solution, the more of it will be fixed on the clay surface, according to the law of chemical mass action. Some species are stronger attracted to the clay than other. The selection depends on the constitution and species of clay and the affinity of the charged particles to remain in the solution. The preference for an species of ions to be taken up by the clay over another ion species, is called cation selectivity. If an ion is held on the clay surface and become displaced by another due to change in its aqueous concentration, the ion is desorbed. If it is desorbed by an ion introduced by the aqueous solution, it is said to be exchanged[14].

¹Lipophilic materials are those that attract non-polar organic compounds, most notably oils, fats, greases, and oily substances. In most cases, synonymous with hydrophobic[15].

Part II

Equipment & Chemical Compounds

Chapter 5

Equipment

5.1 The Cell

To make samples of frozen laponite chains, the cell shown in Figure 5.1 was used. The dispersed laponite was poured onto the cell which was placed on a piece of glass. When the paraffin is cold, the voltage can be turned off and the sample taken out from the cell for observation.

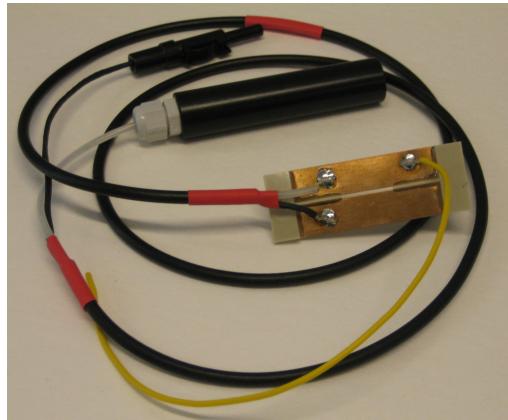


Figure 5.1: The cell. The sample is placed in the 1 mm gap between the two electrodes. The long black pipe is the high voltage contact. The small black contact is the ground contact. The yellow cable is placed on the cell to have the opportunity to measure the actual voltage applied.

The cells were created particularly for these experiments, based on an old similar model. The model had a glass disk glued on beneath the electrodes, and this model was designed with the same intention. Later it was concluded that it

was much easier to remove the finished sample without the the glass disk. The absence of the glass lead to very fragile cells because there is very small areas where glue can be placed, and the cells needed reparation several times. In future experiments the cells should be redesigned to be more robust.

5.2 High Voltage Power-Supply

To achieve the required voltage needed in the experiments a high voltage power-supply was used, shown in Figure 5.2. The in- and out-voltage is proportional where $V_{in} = 0 - 15 \text{ V}$ and $V_{out} = 0 - 5 \text{ kV}$. All experiments were performed at $V_{out} = 2 \text{ kV}$.



Figure 5.2: High voltage power-supply.

5.3 Optical Microscope

To observe and study the samples, an optical microscope, Zeiss Stemi 2000C Stereomicroscope, was used, shown in Figure 5.3 and 5.4.

To achieve additional magnification a 2x supplementary lens, screwed to the objective front lens mount, was available. This supplementary lens was more or less permanently mounted due to one of the light sources, Figure 5.8, which was almost unattachable without the supplementary lens. To handle the samples on the microscope a very simple stage was used, shown in Figure 5.4.



Figure 5.3: The microscope.



Figure 5.4: Close view of the microscope showing the sample stage and the supplementary lens.

5.4 Camera

One of the qualities of the microscope model is the camera port which allows a camera to be mounted on the top of the microscope, and hence let the user utilize a computer monitor for study instead of the eyepieces, which considerable simplify the sample view. The camera model used was a PixeLINK 1.3 Megapixel FireWire Camera PL-A642 (shown in Figure 5.5).



Figure 5.5: The camera[16].

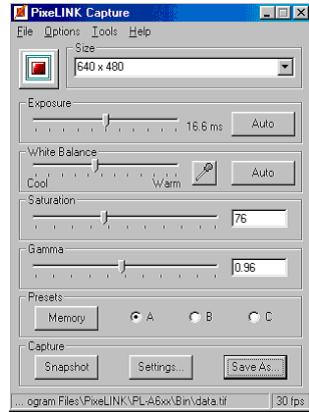


Figure 5.6: The software menu.

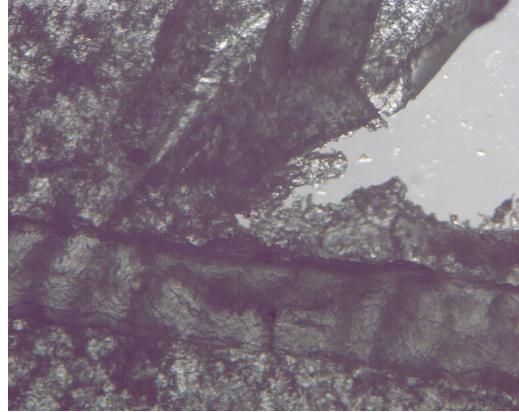


Figure 5.7: A captured picture of laponite in paraffin.

As its name indicates, the camera is connected to the computer with a fire-wire cable. Software included with the camera offers real-time isochronous video streaming and makes it possible to follow the sample continuously, also under movement. The software gives the opportunity to adjust, e.g., the exposure and saturation of the image, but the perhaps greatest advantage of the camera compared to the eyepieces, is the option to take snapshot images of the sample at any time and setting[16]. The software menu and an example of a captured picture is shown in Figure 5.6 and 5.7, respectively. It is also possible to make movies with the camera, in this case, using Windows Movie Maker. Examples of this are shown in the enclosed CD-ROM.

5.5 Light Sources

To observe the samples in the microscope, two different light sources were used. One source illuminates from above Figure (5.8), and one illuminates from beneath Figure (5.9). The pictures taken, when illuminating from above, gave the brightest and best pictures, and therefore was the most used method.

5.6 Heating Plate

The heating plate shown in Figure 5.10 offers a stepless temperature control and a stepless blender function. This is mainly used to heat up the cell and glass plate before use. The purpose of this is to be able to prepare the liquid paraffin without have to worry about solidification. It is also used as a blender and heater under the preparation of laponite with CTAB.



Figure 5.8: The light source used to illuminate the samples from above.



Figure 5.9: The light source used to illuminate the samples from beneath.

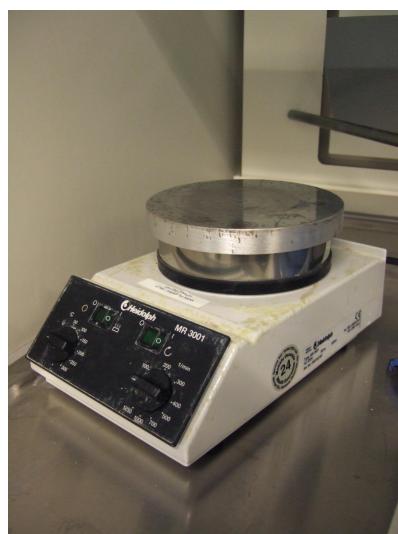


Figure 5.10: The heating plate.

Chapter 6

Chemical Compounds

6.1 Clays

The definition of clays were first given in the nineteenth century based on their particle size, where the particles with extension less than $2 \mu\text{m}$ were called clays. This was the limit of the optical microscope resolution, meaning that every mineral particles beyond this limit were called clays. Although this definition no longer is sufficient, most particles of this order of size belong to the same mineral group and have a lot in common[14].

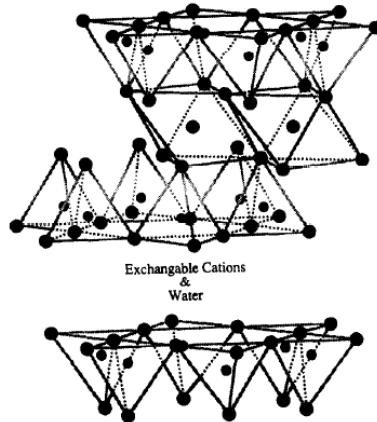


Figure 6.1: The structure of a smectic clay[17].

Clay minerals can take a large variety of forms like amorphous, chain and layered structures. Among these species we have the 2:1 layered silicates, known as the smectics. These are among the most studied clays due to the vast range of

utilizations[17]. The laponite, used in the current experiments, is such a clay species. Figure 6.1 shows the structure of a 2:1 layered smectic clay, i.e. a structure where one octahedral layer is sandwiched between two tetrahedral layers.

6.1.1 Laponite RD

Laponite is a synthetic layered silicate and has the empirical chemical formula $\text{Na}^{+0.7}[\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3}\text{O}_{20}(\text{OH})_4]^{-0.7}$. The layer structure is of the 2:1 type, shown in Figure 6.3. Here we see six octahedral magnesium ions between the two layers of four tetrahedral silicon atoms. These groups are balanced by twenty oxygen atoms and four hydroxyl groups. In a laponite crystal these unit cells are repeated in two directions, resulting in the disc-shaped particle shown in Figure 6.2. It has been estimated that a typically laponite crystal contains 30000 - 40000 unit cells. Particles of this size are called colloids.

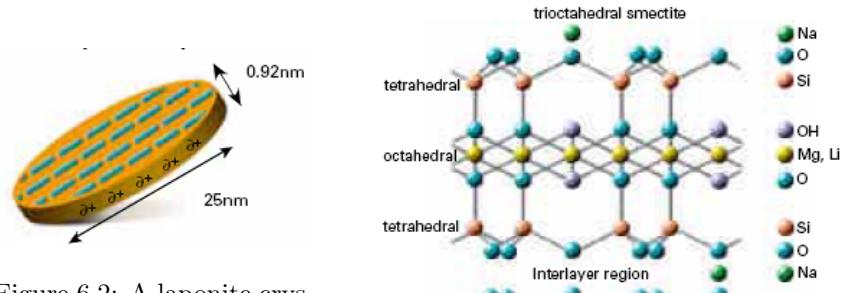


Figure 6.2: A laponite crystal, showing the dimensions and shape.

Figure 6.3: Schematic of a laponite particle.

The negative charged clay particles are neutralised with sodium ions absorbed on the surface, shown in Figure 6.3 and 6.4. Dispersed in water, the crystals are held together in stacks by a combination of electrostatic and osmotic forces, caused by these sodium ions in the interlayer regions (see Figure 6.4). By adding polar compounds, e.g a surfactant, the sodium can be held away from the particle surfaces, and allow cationic exchange[18]. The cationic exchange is made use of in some of the experiments, and is further described in section 4.3, 6.3 and 7.2.

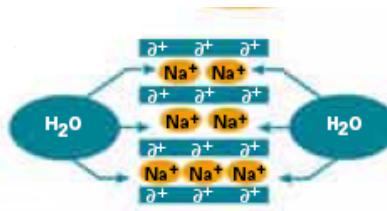


Figure 6.4: Schematic of laponite particles dispersed in water.

6.1.2 Alkyl Quaternary Ammonium Smectite

The AQAS is a modified laponite clay, meaning that it is already made lipophilic, see section 4.2. There was only a small amount of this clay available as a product sample. This clay should be tested, to see if it should be purchased.

6.2 Paraffin

Paraffins (alkanes) is a generic common name for a large number of homologous hydrocarbons which all have the same general chemical formula on the form C_nH_{2n+2} . These have successively higher density and boiling point, where the first four exist as gases in room temperature ($25^\circ C$), and the subsequently paraffins as liquids. When the paraffins contains ~ 25 carbon atoms, they becomes solids. The paraffin wax used in our lab has a number of carbon atoms in this order of magnitude. These waxes are white and partly transparent, as shown in Figure 6.5. The waxes have their melting point in the range $44^\circ C - 58^\circ C$ and a density in the range $0.88 \frac{g}{cm^3} - 0.92 \frac{g}{cm^3}$ [19].



Figure 6.5: Paraffin wax.

The wax consists of mostly straight hydrocarbon chains, between 80 % and 90 %. The balance consists of isoparaffins and cycloparaffins, shown in Figure 6.6.

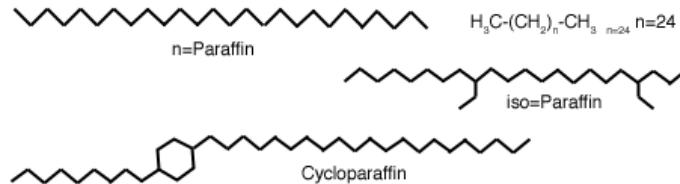


Figure 6.6: Drawing of paraffin wax molecules[20].

Some other general properties of paraffin waxes are[20]:

- Non-toxic.
- Combustible.
- Non-reactive.
- Soluble in ether, benzene, and certain esters.
- Good water barrier.
- Extremely good electrical insulator ($\rho \approx 10^{17} \Omega\text{m}$)[21].

The paraffin wax used in the current experiments is shown in Figure 6.5. This wax has its melting point in the range 46°C – 48°C . It consists of a small amount of impurity sulphate (SO_4) $\leq 0.015\%$.

6.3 CTAB

CTAB - CetylTrimethylAmmoniumBromide has the chemical formula $\text{C}_{19}\text{H}_{42}\text{BrN}$, and is shown in Figure 6.7. It exists as a white solid powder in room temperature. It is a cationic surfactant, and is used to treat the laponite RD to make the clay particles lipophilic (see section 4.3) making it more soluble in paraffin (or oil). The CTAB datasheet tells us that CTAB itself is solvable in ethanol and acetone.

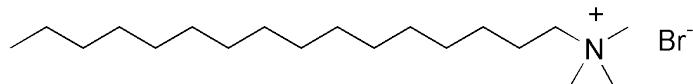


Figure 6.7: Schematic of the CTAB-molecule[22].

Part III

Experiment

Chapter 7

Sample Preparation

7.1 Clay Samples

All of the samples consist of paraffin and clay. As mentioned in the introduction three different kinds of clay samples were investigated. The majority of the experiments were performed using normal laponite (section 6.1.1). Then the laponite was treated with CTAB. This method is in its initial stage and only a very few experiments were performed. The last sample type contains preprepared clay (section 6.1.2). Like the CTAB-prepared clay, this is also an experiment at an early stage. The sample preparation was basically the same for all three kinds of clays. It can be summarized as:

1. Prepare the proper amount of paraffin in a container.
2. Melt the paraffin.
3. Prepare the proper amount of clay and mix it with the liquid paraffin, shaking the container.
4. Pour the dispersed clay onto the preheated cell. (See Figure 8.1 for the experimental setup)
5. Turn on the voltage and the heat off.
6. Let the paraffin solidify, turn off the voltage and cut out the sample.

The concentration of clay used was mostly $\frac{1\text{ g}}{10\text{ ml}} \frac{\text{clay}}{\text{paraffin}}$. This specific amount was chosen to correspond with the concentration used in an experiment of clay suspensions in oil performed by Børge Aune Schjelderupsen. The same concentration was chosen in the two experiments, so an easy comparison could be made, particularly when using paraffin in the rheometer. The exact mass density of the paraffin was unknown. A couple of test were performed and the results gave values at the lower edge of the interval given in section 6.2. The

tests suffered from considerable uncertainty due to losses, so the mass density was set slightly higher, to a value at $0.9 \frac{\text{g}}{\text{ml}}$. Due to fast sedimentation (see section 10.3), the actual concentration of clay in the finished samples was quite unstable and varied from sample to sample, which means that the mass density error played a minor role.

7.2 Preparation of Laponite using CTAB

The properties of CTAB is described in section 6.3 and 4.3. Our goal was to make the laponite lipophilic using CTAB. The procedure to do this was based on an article by Leach and Hopkinson et al.[23], where an analogous experiment was performed using DODAB¹ instead of CTAB. Our experiment was therefore slightly adjusted to fit the use of CTAB. All amounts of materials were half of the amounts used by Leach and Hopkinson et al.[23], since this is just a test of the method. The following procedure was used:

1. Mix the proper amount (400 ml) of distilled water and CTAB (2.5 g) while stirring.
2. Heat to 80 °C and add the proper amount of ethanol (100 ml 20 %) while stirring.
3. Add the stoichiometric amount of laponite (7.53 g) while stirring.
4. Cool the solution overnight, covered and under stirring.
5. Filtrate the solution using 0.2 μm filter.
6. Stir the filtrated clay in a 125 ml half and half distilled water and ethanol solution.
7. Repeat this process (four times).
8. Dry overnight, heated to 100 °C.
9. Pulverize the clay with pestle and mortar.
10. Heat the clay to 100 °C for one hour.
11. Collect the finished clay in an airtight container.

7.2.1 Calculations

The calculations of the stoichiometric amount of clay were carried out based on the decision to use 2.5 g of CTAB.

¹Dimethyl dioctadecylammonium bromide

The cationic exchange capacity (CEC) for laponite is $47 \frac{\text{meq}}{100\text{g}}^2$ [17] = $47 \frac{0.001\text{ mol}}{100\text{ g}}$. In this experiment we decided to use an amount of CTAB corresponding to twice the CEC of laponite[24]. With a molar mass (Mm) of CTAB of $349.39 \frac{\text{g}}{\text{mol}}$, we get the following calculations for the stoichiometric amount of CTAB needed per gram laponite:

$$\begin{aligned} 2 \times \text{CEC} &= 94 \frac{0.001 \text{ mol}_{\text{CTAB}}}{100 \text{ g}_{\text{LP}}} = \frac{0.094 \text{ mol}_{\text{CTAB}}}{100 \text{ g}_{\text{LP}}} \cdot 349.39 \frac{\text{g}_{\text{CTAB}}}{\text{mol}} \\ &= \frac{32.843 \text{ g}_{\text{CTAB}}}{100 \text{ g}_{\text{LP}}} = 0.3284 \frac{\text{g}_{\text{CTAB}}}{\text{g}_{\text{Laponite}}}, \end{aligned} \quad (7.1)$$

where the relation $\text{Mm} = \frac{\text{m}}{\text{n}}$ was used in the calculation.

7.2.2 Unsuccessful Method

Before the method described in section 7.2 were adopted, some initial attempts of cationic exchange were done. These experiments were loosely based on a method described by Nakamura et al.[24]. These experiments did not include neither the predispersing of CTAB nor the filtrating of the unreacted material. We may have destroyed the particles when boiling the solution instead of just heating it when removing the water.

²This value is very uncertain. Different literature gives different values of the CEC, varying from $47\text{-}80 \frac{\text{meq}}{100\text{g}}$ [17, 23, 24]. After consultation with our supervisor, we decided to use $47 \frac{\text{meq}}{100\text{g}}$. As shown by Velde[14], the CEC should be measured at neutral pH, since the surface cation concentration is pH-dependent. This fact may explain the variations in reported CEC-values.

Chapter 8

The Setup

The experimental setup is shown in Figure 8.1. The individual equipment devices used are described in detail in chapter 5. The cell is connected to the high voltage power-supply with $V_{in} = 6$ V, which gives $V_{out} = 2$ kV and $E_0 = 2 \frac{\text{kV}}{\text{mm}}$, a well suited magnitude for ER performance.

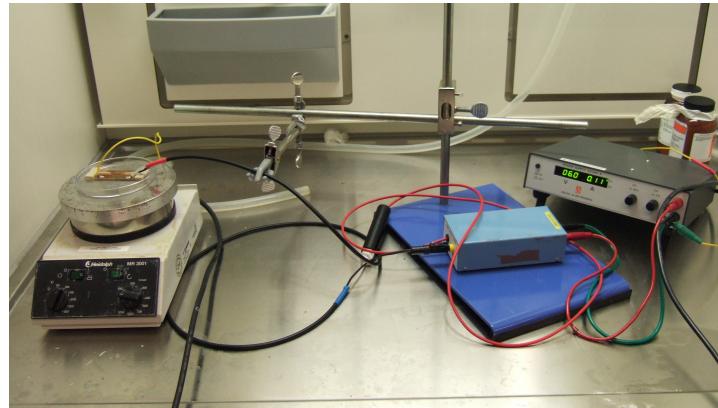


Figure 8.1: The experimental setup.

Figure 8.2 shows a close up of the cell while in use. One can clearly see the clay chain formation between the electrodes. The paraffin is still liquid though, and the chains are not always that easy to see when the paraffin solidify. Figure 9.8 in chapter 9 is a picture taken of the same sample as in Figure 8.2 below.



Figure 8.2: Chains of CTAB-treated laponite in liquid paraffin under the application of 2 kV.

In the experiments the cell was placed directly on the glass surface, as in Figure 8.2. The paraffin sticks very easily to glass and it often occurred problems with removing the cell and the sample without destroying one or both of them. In the very last experiment, a plastic film, called polyimide, was put between the glass surface and the cell to avoid this, which proved to be an excellent material for the purpose.

8.1 Films of the Chain Formation

The enclosed CD-ROM contains five films of the experiment where the microscope camera filmed the course of events. The liquid is silicone oil, not paraffin, since the heating could not be used at the microscope. The first film shows the formation of AQAS chains when the voltage is turned on and slowly increased up to 2 kV. The four last films shows the same liquid as in the first film, when 2 kV is applied immediately. As expected, the finished chains in the films are similar to the ones in Figure 9.7 in chapter 9, showing the same experiment using paraffin. The last film also shows what happens when the voltage is turned off.

Part IV

Results & Analysis

Chapter 9

Results

In all experiments the applied voltage was 2 kV, which should be above the threshold voltage for the ER effect to occur. The 1 mm gap between the electrodes gave an electrical field strength of $2 \frac{\text{kV}}{\text{mm}}$. This field strength is within the field strength interval that is commonly used in ER experiments[1, 7].

Figure 9.1 - 9.5 shows chain formation in laponite RD. The chains can be seen as lines or columns across the sample. In Figure 9.1 - 9.3 the uppermost paraffin surface of the sample was removed to access the laponite chains directly. Figure 9.4 and Figure 9.5 does not have the surface removed and appears quite different visually. Figure 9.6 shows a sample with pure paraffin. It is easy to see the difference between pure paraffin and the clay dispersions. The paraffin sample was created using exactly the same procedure as with the other samples, just that no clay was added in this case.

Figure 9.7 shows chains of AQAS. These chains are more narrow and vague than for laponite RD. Figure 9.8 shows chains of the CTAB modified clay. The chains appears quite different than the RD chains. They are bluish and irregular, although the color is most likely created by the settings of the microscope and the software, and is not the natural color, since no blue color was visible under the experiment (See Figure 8.2).

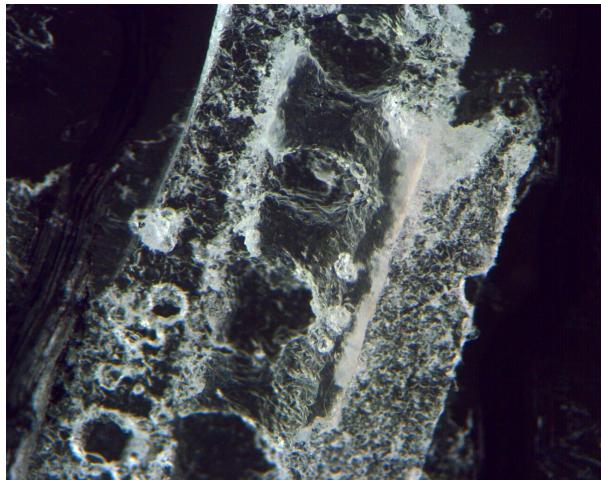


Figure 9.1: Laponite chains formed with 2 kV applied voltage. 20x magnification.

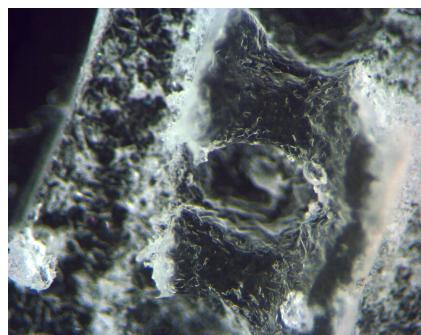


Figure 9.2: Laponite chains formed with 2 kV applied voltage. 40x magnification.

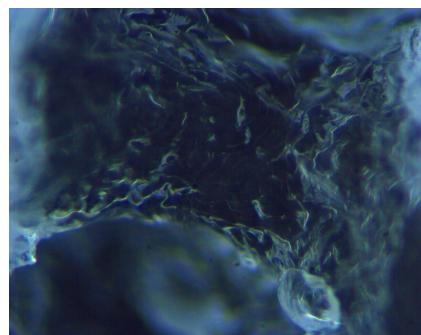


Figure 9.3: Laponite chains formed with 2 kV applied voltage. 100x magnification.

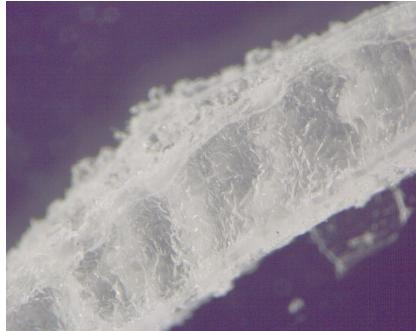


Figure 9.4: Laponite chains formed with 2 kV applied voltage. 25x magnification.

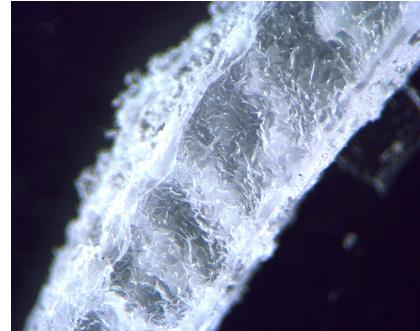


Figure 9.5: Laponite chains formed with 2 kV applied voltage. 26x magnification.

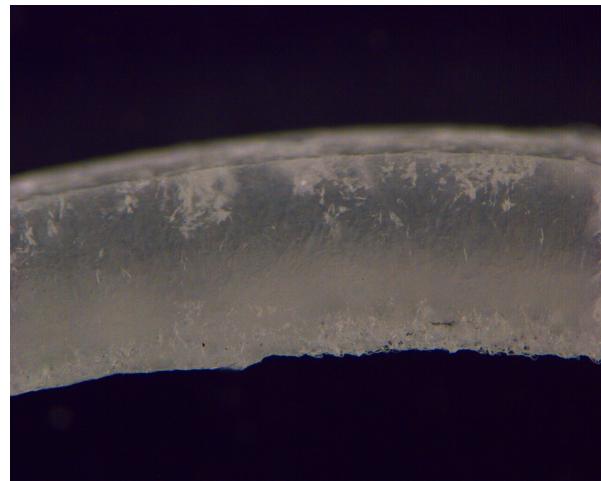


Figure 9.6: Sample of pure paraffin with 2 kV applied voltage. 25x magnification.

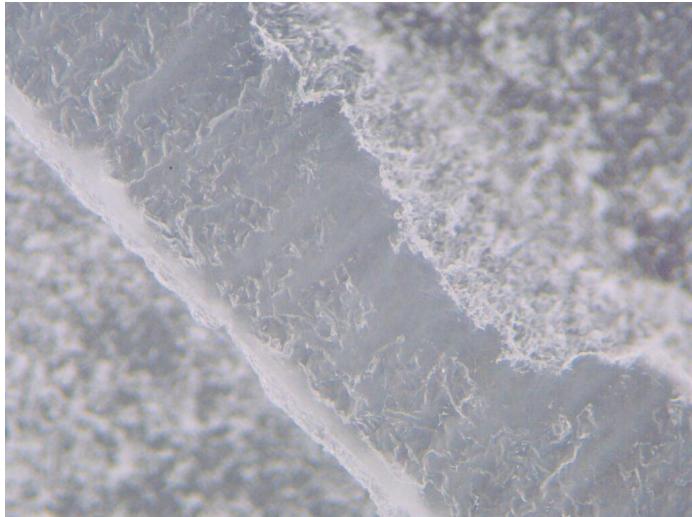


Figure 9.7: Chains of AQAS formed with 2 kV applied voltage. 25x magnification.



Figure 9.8: Chains of CTAB modified laponite formed with 2 kV applied voltage. 26x magnification.

Chapter 10

Analysis

10.1 Clay Concentration

When starting to work with the paraffin and clay, the intention was to have a clearly defined clay concentration in the samples, mostly for comparison reasons. After an early successfully experiment, there occurred major problems in reproducing the results. There was no or very weak ER effect to detect as shown in Figure 10.1. After some time the reason was discovered, viz. fast sedimentation (See section 10.3 for details). When pouring the dispersed solution onto the cell, only some of the liquid was used, naturally the uppermost. A few seconds is enough to sediment nearly all of the clay away from the top of the container. One thus get undetectable ER effect, just because there is very little clay present. This problem was solved by using a pipette, although this led to the possibility of getting a too high concentration of clay where the finished sample will become a pasty mess as shown in Figure 10.2. With some experience, the use of the pipette gave satisfactorily results.

10.2 Paraffin as a Solvent

When starting to work with the paraffin the knowledge of its behavior and properties was very limited. It was chosen based on some specific criteria. First of all, the solvent material should be solid in room temperature at the same time as it should have a low melting point, at least so that it would be possible to melt and handle it with the accessible equipment. The melting point of only just 50 °C fulfilled that requirement. Secondly, it was important that the chemical structure was as easy as possible, to be able to distinguish the clay from the solvent without any major problem. Consisting of no less than 80 % of alkanes, having a white partly transparent color, the paraffin wax was a good choice. In

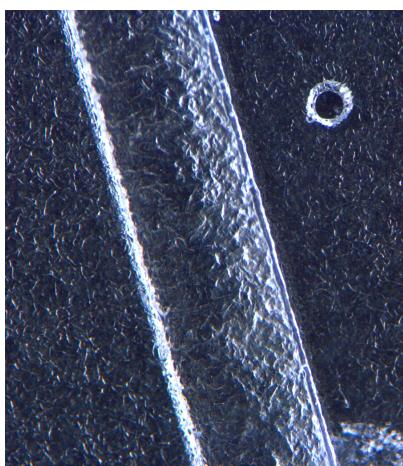


Figure 10.1: Experiment with too low concentration of clay. Possible chains are not observable.

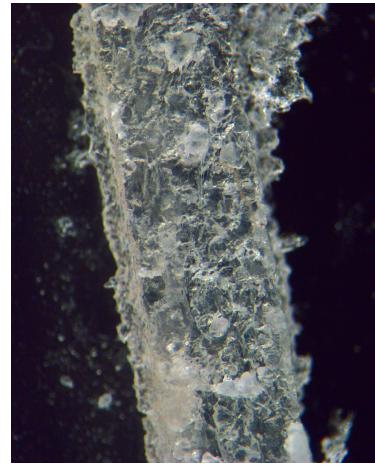


Figure 10.2: Experiment with too high concentration of clay. The sample is pasty and contains no evident chains.

addition, the paraffin was inexpensive, easy accessible and non-toxic. Figure 8.2 shows that the laponite chains are clearly visible when the paraffin is liquid, while the pictures in the result chapter shows that the chains are visible also in solid paraffin.

After thoroughly work with paraffin some inappropriate properties were revealed. Primarily, there were considerable problems with sedimentation as explained in section 10.3. Beyond that, the solid paraffin was perhaps too soft, especially when trying to cut it with a knife or scalpel. This could only be done with considerable difficulties, and the risk of destroying the sample was impending. Finally, the paraffin was hard to remove from the glass and in particular from the cell due to a very sticky surface. The problem with the glass surface was solved as described in chapter 8, but the problem of removing the sample from the cell remained an obstacle.

10.3 Sedimentation

One of the greatest challenges for applications of ER fluids, is the problem with particle sedimentation (See chapter 3). The sedimentation rate increases with rising temperature and since the paraffin needs to be heated to approximately 50 °C to be liquid, as described in section 6.2, sedimentation is expected to occur. In reality, the paraffin temperature used in most experiments was higher than 50 °C, to be able to work with the liquid paraffin in room temperature, and consequently the sedimentation problem increased as well.

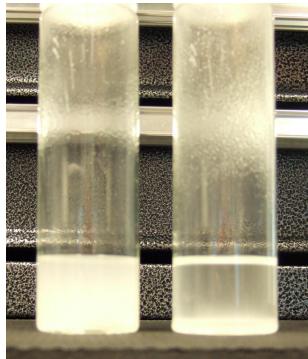


Figure 10.3: Sedimentation at $t = 0$ s.

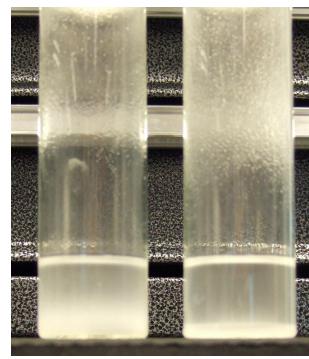


Figure 10.4: Sedimentation at $t \approx 8$ s.

Since the knowledge of the behavior of clay in paraffin was almost non-existing, certain characteristics were assumed a priori to be similar to oil which was studied previously at the laboratory, partly because of the chemical similarities between oil and paraffin, but also because any possible dissimilarities never were thought of. A characteristic that proved both different and important was the sedimentation rate. In oil, the time it takes to sediment the laponite is approximately 15 minutes, i.e. more than sufficient to perform experiments. The sedimentation in paraffin is shown in Figure 10.3 - 10.5. The paraffin was melted at 120 °C. The temperature in the liquid was not measured, but an estimate could be around 80 °C at the time the pictures were taken. The figures shows that the sedimentation is considerable after only a few seconds and almost complete after half a minute. Other tests have shown considerable sedimentation after only one or two seconds. The sedimentation rate has of course much to do with the temperature in the liquid, and this shows the importance of keeping the temperature as close as possible to the freezing point during experiments.

10.3.1 Sedimentation in Modified Clay

When trying to disperse the modified AQAS clay in paraffin, there was discovered that the sedimentation in this paraffin solution was significantly less than for the normal laponite, also at high temperatures (up to 130 °C). The sedimentation in CTAB modified clay was not very different than for the untreated clay.

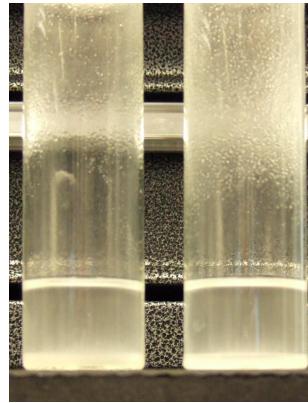


Figure 10.5: Sedimentation at $t \approx 30$ s.

10.4 Paraffin in the Rheometer

In order to test the suitability of paraffin as a solvent for ER performance, the liquid paraffin solution was tested in a rheometer. Two different tests were performed, one sedimentation and one yield stress test. The results of the sedimentation test is shown in Figure 10.6. For comparison, the results of an equivalent test with silicone oil¹ is shown in Figure 10.7.

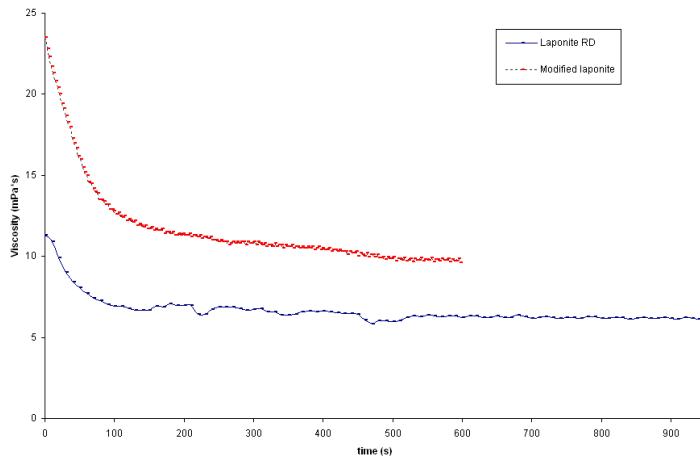


Figure 10.6: The sedimentation of equal concentration of laponite RD and AQAS in paraffin. The RD experiment is performed at 50 °C, while the AQAS experiment at 52 °C.

¹Performed by Børge Aune Schjelderupsen

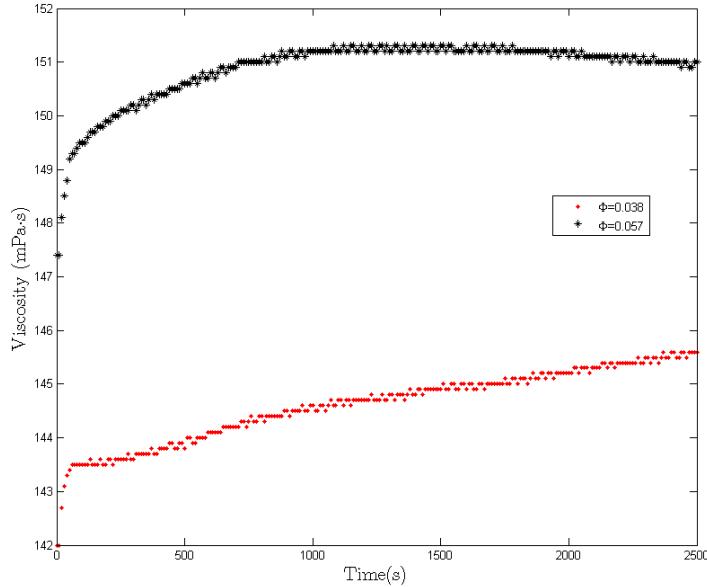


Figure 10.7: Sedimentation of modified AQAS clay in silicone oil. The volume fraction of $\Phi = 0.038$ correspond to the volume fraction used in Figure 10.6

Figure 10.6 shows that the sedimentation for laponite RD is significant after a very few seconds, which corresponds well with other tests. It is also clear that the AQAS sediments much slower and also results in a higher initial viscosity. Comparing Figure 10.6 and Figure 10.7, one discover that the viscosity behavior is dramatically different in oil than in paraffin. The viscosity is very low for pure liquid paraffin, approximately $5 \text{ mPa} \cdot \text{s}$, while it is approximately $100 \text{ mPa} \cdot \text{s}$ for the silicone oil. Studying the evolution over time, one discover that the viscosity in oil does not decrease but *increase*, suggesting very low sedimentation and a stable dispersion. Although the sedimentation is slower in AQAS than in laponite RD, the solution had to be stirred up before the yield stress experiment.

In Figure 10.8 the yield stress for laponite RD and AQAS is shown. Figure 10.9 show the equivalent results for clay in silicone oil.

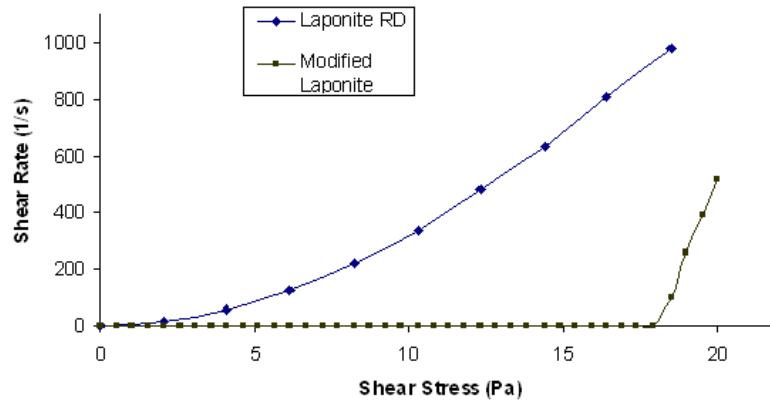


Figure 10.8: The yield stress of two different clays in paraffin. The RD experiment is performed at 60 °C, while the AQAS experiment at 52 °C.

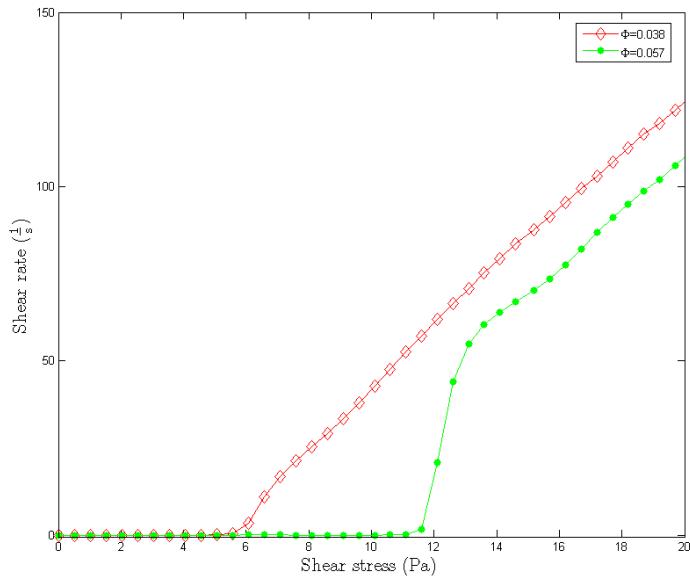


Figure 10.9: Yield stress in silicone oil for AQAS. The volume fraction of $\Phi = 0.038$ correspond to the volume fraction used in Figure 10.8

Comparing Figure 10.8 and Figure 10.9 show that the ER effect is not just apparent for the AQAS in paraffin, but it is actually stronger than it is when solved in oil. The test with laponite RD shows no ER effect at all. Figure 10.8 show that the shear rate increases immediately, indicating no chain formation. This is in accordance with the sediment test, i.e. with most of the clay sedimented (and of course no chains of clay particles). This lack of ER effect can depend somewhat on the temperature used.

10.5 Atomic Force Microscope

Some attempts of studying the paraffin with an atomic force microscope (AFM) were performed. The contact mode was first used with no success. Later, tapping mode equipment were installed on the microscope, a method which is a better approach for the study of soft materials. No evident chains were found, but some pictures proved promising. This should be further investigated in future work.

Part V

Conclusions

Chapter 11

Conclusions

11.1 Paraffin

The melted paraffin proved to be a suitable solvent for clay. Likewise was the paraffin wax appropriate for visual observation of the ER effect. However, paraffin is most likely not a suitable liquid for any ER applications, since the sedimentation rate of the clay seems to be too high. These limitations are probably caused by the initial low viscosity of paraffin, and the requirement for a high operating temperature. Nevertheless, the rheometer experiment with AQAS shows that ER effect in paraffin is present and strong.

11.2 Surface Modified Clays

The AQAS seems to be the most suitable of the used clays. Its sedimentation rate was considerably lower than for the other two types, making it usable with paraffin in rheometer experiments. The chains are narrow and numerous, perhaps indicating a better dispersion than the laponite RD solution, when comparing to the few, wide chains of laponite RD.

The CTAB experiment did not show fully satisfactory results. Its sedimentation rate was high, and quite close to the rate of the untreated clay, and the character of the chains seemed closer to the laponite RD chains than to the AQAS chains. The crushing of the CTAB was probably not good enough, and the clay may also have been heated to much during the production process. The work on this method should be continued in upcoming work.

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