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Capillary forces and osmotic gradients in salt water - oil systems

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Submission date: June 2012
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Preface

This master thesis has been carried out at The Department of Chemistry at The Norwegian University of Science and Technology and in collaboration with Statoil ASA. The report is a result of experimental work tougher with a related literature study.

This is to my knowledge the first time the transport mechanisms in capillary oil-salt water systems have been studied in detail, and therefor it was a lot of trail by error in the beginning of the experiments. However, in the end I got quite comfortable by working with these small tubes and volumes.

There are numerous of people that have helped and supported me along my way to and also through this thesis. In my mind, they all have a little piece in this project. Some more than others, but I am grateful for everything they have done. My family has always been supportive and encouraged me to do what I want, and now I have accomplished one out of many things I want.

Signe Kjelstrup has been outstanding for me in this last year at NTNU, with her knowledge and always welcoming smile. The professor I feared to ask questions to during the lectures in my 2nd year, has now become the person I prefer to ask for help. She has been curtail for me in the last year at NTNU, and for that I will always be in grateful.

Kristian Sandengen and Statoil ASA have supported this project financially, and have also been the creator of this project. I thank you for the support and I hope the project can contribute to future work for Statoil and the Vista Program.

Abstract

This project looks at the capillary systems with salt water and oil that can be found in porous stones in oil reservoir. The interactions between the different phases and how salt concentration differences can move the oil. The first problem was to find how the water migrates from one side of an oil droplet to the other due to the concentration difference. This was discussed, but not experimentally verified. The reason for this is the high inaccuracy of the experiments and the lack of knowledge before starting. However, this project gives a lot of important knowledge about the problem, and good suggestions for improvements.

It was experimentally confirmed that oil is moving due to the difference in salt concentration. From this, the diffusion coefficient was found and reported to be $D = (1.08 \pm 0.10) \cdot 10^{-7} \frac{m^2}{s}$ for glass capillary tubes of radius $0,70$ mm and at $60^o C$, calculated from the phenomenological coefficient L that was found. It was also confirmed that the capillary force does not contribute significantly for this size of the tubes, and therefore L should be independent of the radius.

The maybe most interesting result of the experiments and calculations is that the capillary force will contribute significantly to the total force and then also the movement of the oil droplet. This does not happen before the radius of the tubes where under $0,20$ mm. The experiments and the estimates agreed well with the radius where the change happens.

Sammendrag (Norsk)

Denne masteroppgaven ble gjort for Instituttet for Kjemi ved NTNU i samarbeid med Statoil ASA. Hensikten med forsøkene var å finne transportmekanismen for vann når det passerer olje inne i kapillarsystemer. I dette tilfellet ble det sett på oljedråper innesperret mellom vann faser med ulik natriumklorid konsentrasjon. Dette for å simulere om saltgradienter kan påvirke og forårsake bevegelse av oljedråper. Samtidig vil kapillarkrefter kunne spille en viktig rolle siden systemene er svært små, med radius fra 0,13mm og opp til 0,70mm.

Kraften fra den osmotiske gradienten ble beregnet fra damptrykket til de ulike vann løsningene og er presentert i Tabell 5.1.1. Bidraget fra kapillarkreftene ble estimert på bakgrunn av noen realistiske antagelser, som funksjon av menisk radiusen til oljedråpen. Dette er presentert i Figur 5.2.1, mens den totale estimerte kraften er presentert i Figur 5.5.2.

Det ble gjennomført flere forsøk hvor kapillarrørene var av samme type, men med ulike saltkonsentrasjoner. Figur 2.1.1 viser en skisse av oppsettet med de ulike fasene indikert. Ved å la saltvannskonsentrasjonen variere kunne effekten fra den osmotiske gradienten vurderes og da også den fenomenologiske koeffisienten, se Likning 2.4.10 og Figur 5.3.1.

Det ble også gjennomført forsøk med tre forskjellige tykkelser på kapillarrørene; 0,13mm, 0,26mm og 0,70mm. Dette for å kunne skille om vannet beveger seg langs med veggene og dermed rundt oljedråpen, eller om det diffunderer igjennom. Ved å endre på rør tykkelsen og gjøre målingen av vannfluksen, vil man kunne se om den er proporsjonal med r, for bevegelse langs veggene, eller r^2 for bulk diffusjon. Det var ikke mulig å gi en konklusjon basert på resultatene fordi variasjonen av målingene var svært høy og siden det burde vært gjort målinger ved flere ulike tykkelser på rørene for å gi en bedre regresjon av resultatene. Resultatet er presentert i Figur 5.4.1.

For å finne ut om, eventuelt hvor mye, kapillarkreftene medvirker ble vannfluksen plottet mot radiusen. Dette skulle gi en rett linje med stigningstall 0 om ikke kapillarkreftene medvirket. Figur 5.5.1 viser dette plottet, og slik som tidligere estimert virker det som kapillarkreftene har en innvirkning når radiusen bli under 0,20 mm.

Konklusjonen av prosjektet er at den osmotiske gradienten helt klart vil flytte på oljedråper i kapillarsystemer, men også kapillarkreftene vil spille en rolle når radiusen blir liten nok. Den nøyaktige overgangen vil nok variere litt, men ble estimert til å være rundt 0,20 mm. Andre mer praktisk relaterte spørsmål ble også diskutert, som hvordan denne kan relateres til porøse kapillarsystemer i oljereservoar.

Contents

1 Introduction

The aim of the project is to find out more about transport mechanisms and forces in capillary salt water - oil systems. Why and how does the oil move in these small and narrow systems?

The reason for studying these problems can easily be represented by money. The recovery of an oil reservoir is rather low, normally from 20% up to 35% - 45% with the use of secondary recovery[1] [1]. The so called EOR[2] can furthermore increase the recovery to 60% [2]. The EOR is a general name for processes that changes the physical and/or chemical properties in the reservoir to make it easier for the oil to come out, and within this term is adding chemicals. One usually add chemicals for lowering the interfacial tension around the oil droplet, to make it move easier. This brings the problem back to this project, to find out more about the effect of sodium chloride in the water that is in contact with the oil.

There has already been done experimental work on the effect of osmotic pressure in salt water/oil/water systems. Wen et al. [3] investigated how osmotic pressure influences the migration of water in double emulsion systems. In this case there was a water bubble with low salt concentration that was almost in contact with another high salt concentration water bubble of a greater size, just separated by a hydrophobic layer. Wen et al. observed that the low concentration bubble shrunk, meaning there was a migration of water from this bubble. This was happening until the two bubbles had reached equilibrium, and the osmotic gradient was zero. By looking at the size of the bubbles before and at equilibrium together with the initial concentrations, they could conclude that the salt does not migrate, only water. They also say that in equilibrium the bubbles have the same curvature. However, this is just transport through thin hydrophobic films and Wen et al. concluded that the migration is mainly via a hydrated surfactant mechanism. The water has no other way to leave the droplet than breaking down the film or diffuse through according to Wen.

Cheng et al. made a study of how ions can transport through oil phase [4]. This again is movement from one water droplet to another, but with an oil phase in-between. They had sodium chloride in one of the droplets and silver nitrate in the other, and observed if there was any sedimentation of silver chloride. They showed that the thickness of the surfactant layer is critical for the transportation of ions as micelles through the oil phase, with what seemed to be an optimum depending on the ion that was transported. The Pauling radii was used to describe the size of the ions, and the large ions tended to move slower, likely because they need more surfactants to create a micelle. They further stated that the transport rate of ions is independent of the thickness of the oil phase, with one exception when there is no visual oil phase between the two water droplets, just a double surfactant layer. Then the transport was slower. The conclusion of the experiments is that

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[1] Adding an artificial driving force when the natural pressure is too low

[2] Enchanted oil recovery

there is a reverse micelle transport mechanism, where ions are surrounded by water and then a surfactant layer is diffusing through the oil phase. The formation of micelles is the limiting factor for the transport, and water and/or ions do not break through the surfactant layer and diffuse alone. This means that micelle formation is more important than the osmotic gradient for systems with surfactants at the interface. Even though this is quite different from the system studied in this project, it is worth nothing that ions do not transport without being surrounded by the surfactants, this will be assumed in the experiments for this project.

The force due to a chemical potential gradient is a strong force, so strong that it can be used for a power plant, already done at Tofte in Norway, by the energy company Statkraft [5]. The forces in capillary tubes are of course at a very different magnitude, but so are the required forces to move oil droplets as well. However, it is important to not forget the capillary forces, and at some point when the radius is very small they will contribute. In this project I will look at both forces and separate them by plotting the results.

This project is done on behalf of Statoil, one of the biggest actors in the oil industry, with the interest of learning more about the small and narrow systems inside the oil reservoir. Previously experiments conclude that osmotic gradients can lead to migration of water, even through oil phase. The capillary force does not influence in these experiments, but for this project I will try to look at the magnitude of the capillary force and the osmotic force together, to better understand how water can migrate inside porous stones filled with oil.

2 Theory

The goal of the project is to answer the questions mentioned in the introduction; do osmotic gradients effect the movement? How does the water move? How will the capillary force contribute? The upcoming subsections will go in more detail about the physical properties and forces in a system like this, but first one has to look at the actual case for this project.

2.1 Description of the system

To simulate the movements in a porous stone containing saltwater and oil, I have filled capillary tubes with an organic compound and water of different salinity, Figure 2.1.1. The two phases a and e are the same water solutions, and both are directly connected to the bulk phase around the tubes. In this way the concentration can be assumed to be constant and the same for the two. The high salinity phase in the middle, c, is also a water solution, but with higher concentration of sodium chloride. This will create differences in chemical potential and surface properties for c with respect to the other two water phases. The two oil droplets, b and d, separates the high salinity solution from the low. They can be looked at as membranes that can be selective in the transport of molecules, a little like the membranes used in osmotic power plants and fuel cells. One of the questions for this project is how the oil phase is transported.

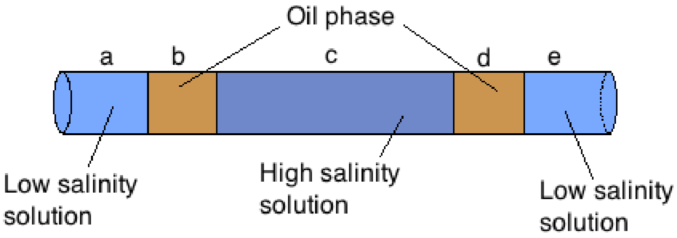

Figure 2.1.1: Sketch of the capillary tubes with letters assigned to the different phases

A setup like this will create forces that wish the oil droplets to move away from each other, assuming that the water migrates easier than the sodium chloride ions as mention earlier. Also a capillary force could work in this direction. If one just measures a system like this it will be impossible to say what causes the movement. However, by doing series of experiments with small changes in the system it may be possible to distinguish the two forces. Figure 2.1.2 shows the forces that play a vital role in a system like this.

The first idea for distinguishing the two forces, has been to change the walls of the tube, which will only change the capillary forces. The weakness of this is that it

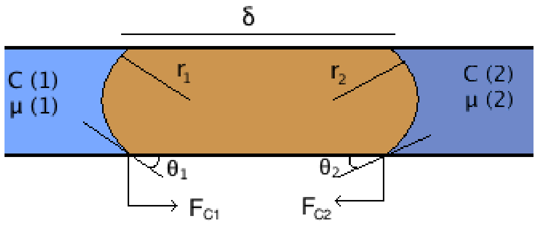

Figure 2.1.2: Sketch of the forces working on the droplet together with important variables that is frequently used in this project

might change the mechanism as well. It is likely that the migration will be effected if the walls were highly hydrophobic or hydrophilic. This is important to keep in mind when relating the results to an actual oil reservoir where the walls are made of porous stone. Zhou et al. have studied the importance of wetting for the porous stones when it comes to oil recovery, and found it to be important [6]. However, they do not study the transport mechanism so it is impossible to say weather it is the same for all the experiments or if it changes with different wetting conditions.

2.2 Chemical Potential

A part of the chemical potential can be compared to "a measure of the potential that a substance has to produce in order to alter a system" according to Atkins [7]. It can be compared to other potential energies such as gravitational and electrical potential energy that causes something to move because it is in a different energy state with a reference to something else. Mathematically it is dependent on a lot of variables and therefore can be described as different partial derivatives, all depending on what variables that are kept constant. For this project I want to vary the concentration and that is why I have chosen to define the chemical potential from the Gibbs' energy, Equation 2.2.1

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{2.2.1}$$

According to Atkins the Gibbs' energy for a gas can be expressed as following, relative to the standard state at 1 bar [7].

$$G = nG_m^0 + RT\ln\left(\frac{P_{vap}}{P^0}\right) \tag{2.2.2}$$

Where R and T are the universal gas constant and the temperature in Kelvin respectively. Using Equation 2.2.1 and the fact that $\mu_{vapor} = \mu_{liquid}$ for systems that are in equilibrium, one will get an equation that is more suitable for this project, Equation 2.2.3. The pressure ratio can also be expressed in terms of the activity $P_{vap}/P^0 = a_i$, where P_{vap} is the vapor pressure for the solution and P^0 is the reference pressure, in this case for pure water. The activity is maybe more logic to use for liquid-liquid systems, but there will always be a theoretical vapor pressure over a solution even though there is no gas phase.

$$\mu_i = \mu_i^o + RT\ln(a_i) \qquad \Rightarrow \qquad \Delta\mu_i = RT\ln\left(\frac{P_{2,vap}}{P_{1,vap}}\right) \tag{2.2.3}$$

The change in chemical potential, $\Delta\mu_i$, of the solvent when adding salt is usually negative and this is also the case for sodium chloride. The more one adds the larger is the decrease in chemical potential [8]. An important thing to notice is that the chemical potential difference depends on the temperature. This means that the force caused by chemical potential is getting larger just by increasing the temperature, and the difference could be significant because it is directly proportional to the temperature in kelvin. The temperature dependence of the permeability is somehow still unknown and can also influence the movements.

The vapor pressure was found by calculation from the osmotic coefficients [9] [10]. It should be mentioned that the osmotic coefficients were originally calculated from the vapor pressure but the vapor pressure it self was not reported. A further description of the calculations can be found in Appendix A together with all data tabulated. Figure 2.2.1 shows the vapor pressure at different sodium chloride concentration and Equation 2.2.4 is a regression of the plot, where c is the concentration.

$$P_{i,vap} = 66,664c_i^2 - 2093,6c_1 + 19934 \tag{2.2.4}$$

The plot goes all the way to the solubility limit of sodium chloride at a temperature 60^oC, and it is even valid for slightly over saturated solutions. This gives raise to a chemical potential difference of up to 1,62 kJ/mol, according to Equation 2.2.3. Table 5.1.1 shows the other chemical potential differences used in the experiments.

2.3 Surface tension and contact angles

A very important aspect in capillary systems is the interactions that happen at the surface between the different phases. The systems in this project have different sodium chloride solutions of various concentration, oil in form of octane and the wall of the capillary tube. For the individual surface tension of the liquids there are two main factors that contribute, namely dispersion forces and interaction forces specific for the different liquids, Equation 2.3.1. Another and more general name for these forces is Lifschitz - van der Waals forces, and it includes all the forces that contributes to the surface tension [11].

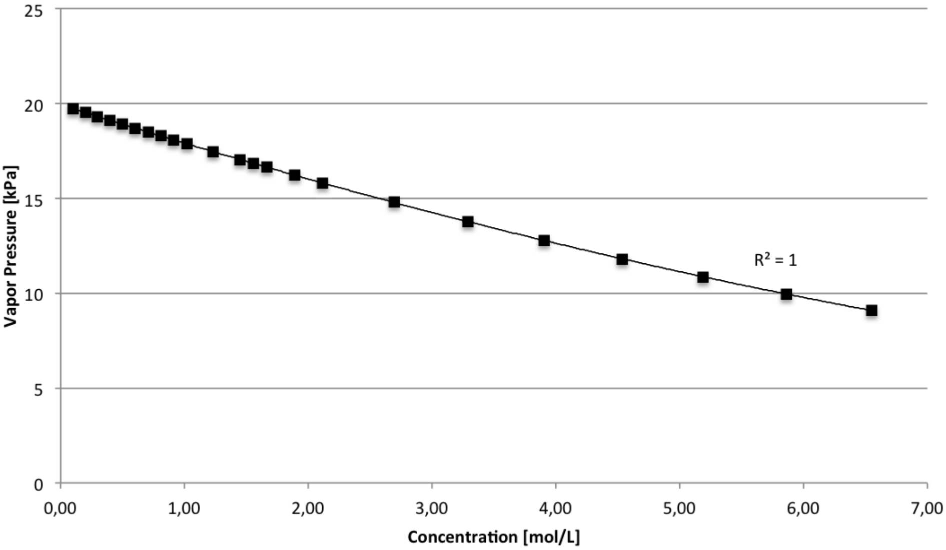

Figure 2.2.1: Plot of the vapor pressure versus the sodium chloride concentration for solutions at 60^oC.

$$\gamma = \gamma^{disp} + \gamma^{sp} \tag{2.3.1}$$

The γ^{sp} term can for instance be due to hydrogen bonding like in the discussed system. For water and dilute water solutions the hydrogen bonding together with the dispersion forces will be dominant, and other effects can be neglected. However, when the salt concentration increases also the salt ions contribute significantly to the surface tension. Experiments show that the contribution of sodium chloride ions leads to an increase in the surface tension [12] [13].

For the octane phase it is more simple, because according to P. C. Mørk [11] the specific forces can be neglected for non polar hydrocarbons and the total surface tension is therefor equal to the contribution from the dispersion forces.

$$\gamma^{sp} = 0 \qquad \Rightarrow \qquad \gamma_{octane} = \gamma^{disp} \tag{2.3.2}$$

Surface tension is usually measured when a liquid is in contact with a gas phase, normally air. The reason for this is that the influences to the surface tension of the liquid, that is caused by the air/gas, can be neglected and thereby one can measure surface tension for each individual substance alone. In other cases, like this project, there is no gas phase, but rather two liquid and one solid phase. This is a more common systems in our everyday life, and in this case the surface tension of a substance is then relative to what it is in contact with. Interfacial tension is the term used for distinguishing between the two types of systems. Interfacial tension describes the same phenomena with the same laws of physics, but is used for liquid-liquid systems and will be used in this project. One rule is that the interfacial tension will always be lower than the highest surface tension for the individual substances in contact. Table 2.3.1 shows some of values that will be of interest for this project with some additional values that are useful for comparisons. It was said that for non polar hydrocarbons the surface tension was only dependent on the dispersion forces, but if an alcohol group is introduced, octanol, the surface tension gets higher. This is most likely due to the possibility for hydrogen bonding, confirmed by the fact that it's interfacial tension to water is lower than the surface tension. Clearly there are some kind of bondings across the interface region that makes it weaker. The values in the table are for the substances at 20 °C, and in general the surface tension decrease with increasing temperature [13].

Table 2.3.1: Tabulated values of surface tension and interfacial tension against water at 20°C [11]

Liquid	Surface Tension [mN/m]	Interfacial Tension against water [mN/m]
$Water$	72.8	–
$Water\ solution(1.0 M NaCl)$	74, 4[13]	–
$Water\ solution(2.7 M NaCl)$	77, 9[13]	–
$Octane$	21.8	50.8
$Octanol$	27.5	8.5
$Ethyleter$	17.1	10.7

The interfacial tension can be estimated from Fawkes equation, 2.3.3. The dispersion forces here contribute in a negative order to the interfacial tension while other specific forces contribute in a positive order. This means that for instance the hydrogen bondings in water will give raise to a high interfacial tension. From the values in Table 2.3.1 it is possible to estimate how much the hydrogen bonding contributes to the resulting interfacial tension for water-octane solutions, $\gamma^{d}_{water} =$ 22.0 mN/m and $\gamma^{sp}_{water} =$ 50.8 mN/m.

$$\gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma^{d}_{A} \cdot \gamma^{d}_{B})^{\frac{1}{2}} \tag{2.3.3}$$

As already mentioned, water with sodium chloride ions have a higher surface tension, and from Fawkes equation one can see that this will influence the interfacial tension between water and octane. It is worth noticing that adding sodium chloride will change the γ_{water} but it might change the γ^{d}_{water} as well. This means the change in surface tension of water will not necessarily be the same as the change in interfacial tension between water and another compound. It depends if the change in surface tension of water is caused by a change in the γ^{d} or γ^{sp}.

A more detailed description of the change in surface tension due to adding a solute can be seen from the Gibbs adsorption isotherm equation. Before this is introduced, it is necessary to define the surface excess, Γ. It can be looked at as a surface concentration, so a two dimensional concentration on macroscopic level.

$$\Gamma_i = \frac{N_i^\sigma}{A} \tag{2.3.4}$$

Where N_i^{sigma} is the number of molecules and the denotation σ indicates that it is on the surface, A is the surface area. The surface can be defined as the small volume where the concentrations are changing with respect to the bulk phase. In this region again one can place a plane without any volume, usually referred to as Gibbs' dividing interface. The surface excess depends on where this plane is actually placed and is a very useful variable for describing a surface. Figure 2.3.1 shows an example for a one component system with two phases, and Gibbs' dividing interface is defined such that $\Gamma = 0$ [14]. This is of course at a molecular level were the distances are very small, but on a microscopic level the surface will look like a plane without any volume.

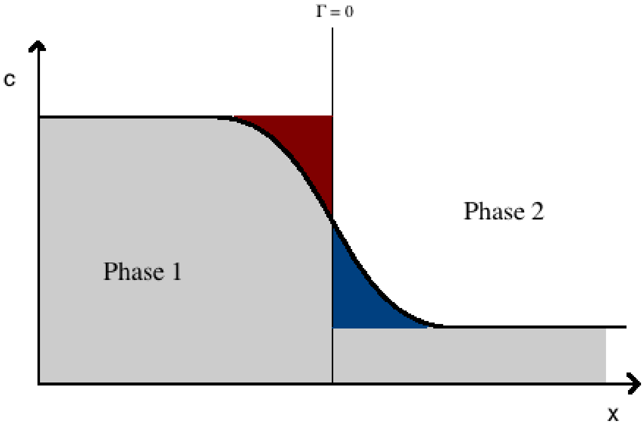

Figure 2.3.1: Ideal placement of the Gibbs dividing interface for one component system with two phases.

The surface line can be chosen freely, but for a single component system it is likely to place it in the middle of the interfacial region. That is sometimes referred to as the perfect surface because each of the phases have the same amount of molecules, within the interfacial region, on each side of the defined surface. For this kind of surface the surface excess is defined as zero, $\Gamma_i = 0$. Sometimes it is convenient do define the surface line differently and then the surface excess will be different from zero, example Figure 2.3.2. This will be the relative adsorption, meaning that the surface excess is relative to the other component(s) in the system, mathematically expressed in Equation 2.3.5.

$$\Gamma_i^{(1)} \equiv \Gamma_i^{\sigma} - \Gamma_1^{\sigma} \frac{c_i^{\alpha} - c_1^{\beta}}{c_1^{\alpha} - c_1^{\beta}} \tag{2.3.5}$$

Where the notations α, β and σ indicate the the bulk phase 1, bulk phase 2 and the interfacial region of the system.

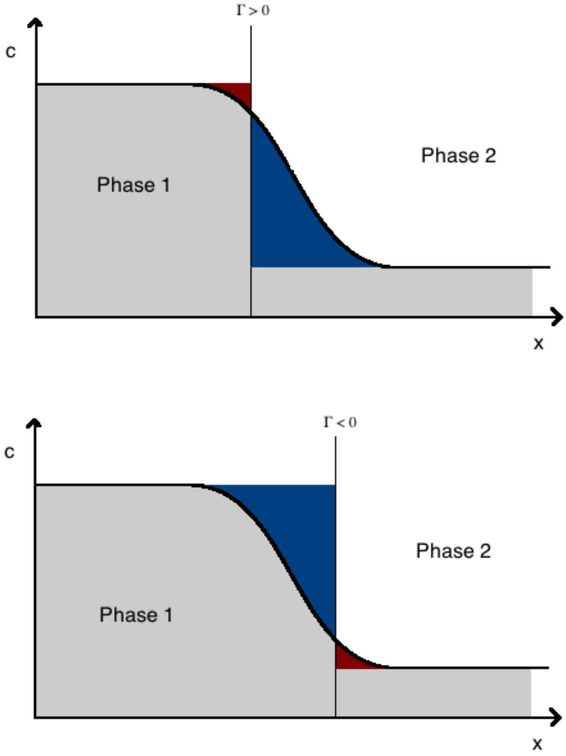

Figure 2.3.2: Two possible placements of the Gibbs dividing interface that makes the surface excess different from 0

In this project it is a multi-component system with water, sodium chloride and octane. When there is a solution with two components there will also be two components present at the surface. Depending on how they interact with the other phase, it might not be a continuous concentration drop in the interfacial zone for both of the two components, an examples can be viewed in Figure 2.3.3. If the relative concentration profile in the interfacial region is different it will be impossible to find a perfect surface line where $\Gamma_i = 0$ for both. This brings it back to Gibbs adsorption isotherm equation which says that the change in surface tension is a linear combination of the changes in chemical potential.

$$d\gamma = -\sum \Gamma_i d\mu_i \qquad \Rightarrow \qquad d\gamma = -\Gamma_w d\mu_w - \Gamma_{NaCl} d\mu_{NaCl} \tag{2.3.6}$$

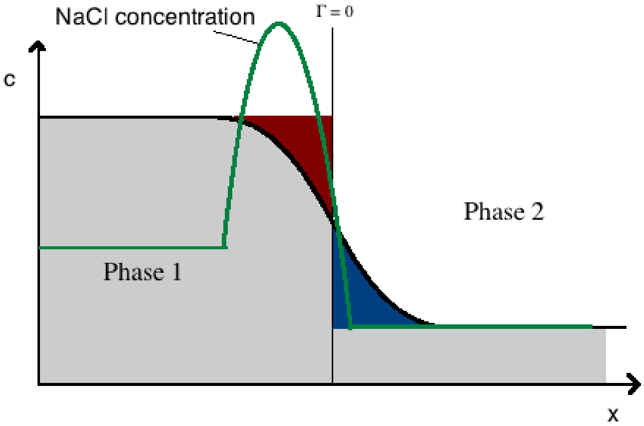

Figure 2.3.3: Example of a multicomponent system where a solute is enriched just under the surface

The expression simplifies a lot by defining the surface so that the $\Gamma_w = 0$, meaning that the surface is defined by the water concentration in the interfacial region without thinking of the sodium chloride. Then taking the derivative of Equation 2.2.3 and inserting it into Equation 2.3.6 gives the following equation.

$$\Gamma_2^* = -\frac{a}{RT}\frac{\partial \gamma}{\partial a}\bigg|_T \tag{2.3.7}$$

A very important equation which tells directly that solutes that enrich the surface will give a lower surface tension than the pure component and vice versa. As earlier mentioned sodium chloride gives a higher surface tension, which means it does not enrich the surface. In reality there are two interfaces, one for the water and one for the sodium chloride. It is normal for highly polar solutes such as ions to increase the surface tension of water, while most other non-polar solutes will lower it [14].

The force due to surface tension is usually referred to as the capillary force. For this project I have chosen a little different approach starting out with the partial molar pressure dependent Gibbs' energy, Equation 2.3.8.

$$\frac{\partial \bar{G}_1}{\partial P_1} = \bar{V}_1 \tag{2.3.8}$$

In the system there will be a pressure difference from one side of the oil droplet to the other. This is because the surface tension of the two water solutions will be different and lead to different curvature of the meniscus. From Young-Laplace's equation, 2.3.9 one can see that a different radius of the meniscus will lead to a pressure difference that will be a contributing force to the movement of the oil droplet.

$$\Delta P = \frac{\gamma_i}{R_1} + \frac{\gamma_i}{R_2} \qquad for\ R_1 = R_2 \qquad \Delta P = \frac{2\gamma}{R} \tag{2.3.9}$$

Where R is the radius of the menisci, and ΔP is the pressure difference over the meniscus of one side of the oil droplet. A combination of Young-Laplace equation for each of the sides, gives the pressure difference over the whole droplet. Integration of Equation 2.3.8 from one side of the meniscus to the other, and the use of Young-Laplace equation, will give an expression of the free energy

$$\Delta G = V_m \left(\frac{2\gamma_i}{R} \right) \tag{2.3.10}$$

This equation will be usefull when describing how the capillary forces will contribute to the movement of the oil droplet. This will be further discussed in the upcoming section together with the contribution from osmotic gradients.

In the end I want to introduce Young's equation which gives a relation between the surface tensions and the interfacial tension, Equation 2.3.11. It also relates the contact angle to the different surface/interfacial tensions.

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos(\theta) \tag{2.3.11}$$

2.4 Driving Forces

For this project I have chosen to look at the local entropy production, and defining the local entropy production in the oil phase as the contribution from the capillary force. The movement is dependent on either the osmotic force, $\Delta\mu_w$, or the pressure difference cause by difference in interfacial tension and curvature, $\Delta\mu_c$, or a combination of the two. This gives two equations, but one must remember that the change in chemical potential and the capillary force are related. Meaning that if one of them changes the other one will as well. The two equations bellow describe the local entropy production for the system

$$\sigma_w = J_w \left(-\frac{1}{T}\frac{d\mu_w}{dx} \right) - J_{NaCl} \left(\frac{1}{T}\frac{d\mu_{NaCl}}{dx} \right) \tag{2.4.1}$$

$$\sigma_o = J_w \left(-\frac{1}{T}\frac{d\mu_c}{dx} \right) \tag{2.4.2}$$

Where subscript w indicates water, o oil and c capillary force. Every sodium and chloride ion will be carrying some water molecules around due to their electrical charge. This will slow down the movement and also prevent the ions from moving through or around the oil phase. For the project I have assumed that there is no flux of sodium chloride. This have been verified experimentally for a similar system by Wen et al. [3]. If J_{NaCl} is equal to 0 then the last term can be removed from the Equation 2.4.1. The entropy production defines fluxes, and their conjugate forces. And according to Onsager, the flux is proportional to the forces multiplied by a constant [15]. Meaning that the water flux can be expressed as following

$$J_{water} = -L\frac{1}{T}\left(\frac{d\mu_w}{dx} + \frac{d\mu_c}{dx}\right) \tag{2.4.3}$$

Where L is the phenomenological coefficient. The total local entropy production will be the sum of the local entropy production equations 2.4.1 and 2.4.2 , and by integration over the distance one will get the total irreversible entropy production. This will be the entropy production over one oil droplet.

$$\frac{S_irr}{dt} = \int_0^l \sigma_w + \sigma_o dx = -J_w\frac{1}{T}\left[\frac{\mu_{w,l} - \mu_{w,h}}{\delta} + \frac{\Delta\mu_c}{\delta}\right] \tag{2.4.4}$$

Where the $\mu_{w,h}$ and $\mu_{w,l}$ mean the chemical potential of water phases with high and low salinity respectively. This have been explained earlier and they can be expressed according to the Gibbs' equation 2.2.3.

The $\Delta\mu_c$ is still unsolved and hard to estimate, but with use of the theory explained in the previous section it is possible to expressed in terms of measurable variables. These kind of measurements requires apparatuses of high precision and thereby too expensive to use for this project. The equations can still be derived completely free. When the oil droplet is in contact with two surfaces with different surface tensions, there will be a constant difference in pressure at each side. One can look at the difference in curvature and calculate the capillary force or simply just multiply the pressure difference with the molarity of the oil to get a force, which I have chosen to call $\Delta\mu_c$.

$$\Delta\mu_c = V_o[P_{o,h} - P_{o,l}] \tag{2.4.5}$$

Where the two pressures in the oil are distinguished by h (high) and l (low) to indicate the concentrations in the surrounding solutions. Then by adding and subtracting the pressure in the water phase, P_w, gives an equation with similarities to Young-Laplace equation 2.3.9.

$$\Delta\mu_c = V_o[P_{o,h} - P_w \quad - \quad P_{o,l} + P_w] \tag{2.4.6}$$

There are two pressure differences which are related to each of the curved interfacial surfaces of the oil droplet, and therefore the Young-Laplace equation can be applied. However this equation is for spheres, tubes, droplets and other similar geometries.

In this project it is not the surface tension relative to the center of the curvature of the interfacial region, but its contribution to the movement along the walls. This will be compensated by multiplying with the cosine to the contact angle, θ (see Figure 2.1.2). So by combining Equation 2.3.9 and Equation 2.3.10 and including the cosine to the angle one get an equation for the capillary force.

$$\Delta\mu_c = V_o\left[\frac{2\gamma_{w,h}\cos(\theta_h)}{r_h} - \frac{2\gamma_{w,l}\cos(\theta_l)}{r_l}\right] \tag{2.4.7}$$

Where $\gamma_{w,i}$ is the interfacial tension between the oil phase and the water for the different concentrations, i. It can be written a little different with the use of Young's equation 2.3.11.

$$\Delta\mu_c = 2V_o\left[\frac{\gamma_{o,s} - \gamma_{w,h,s}}{r_h} - \frac{\gamma_{o,s} - \gamma_{w,l,s}}{r_l}\right] \tag{2.4.8}$$

Where the last subscript s indicates that it is against the solid surface, in this case glass. All of the surface tensions against solid are unknown, so it will be very hard to predict this force.

This brings the problem back to Equation 2.4.3, so the water flux can be expressed as following for migration from phase a to phase c. The very same situation will be for the transport from e to c.

$$J_a = -L\frac{1}{T}\left[\Delta\mu_w + \Delta\mu_c\right]\frac{1}{\delta_b} \tag{2.4.9}$$

δ_b is the thickness of oil droplet b. And to write the final expression including the simplification mention earlier and the derivation done, it will gives this

$$\begin{aligned} J_a &= -L\frac{1}{T}\left[RT\ln\left(\frac{P_{2,vap}}{P_{1,vap}}\right) + 2V_o\left\{\frac{\gamma_{o,s} - \gamma_{w,h,s}}{r_h} - \frac{\gamma_{o,s} - \gamma_{w,l,s}}{r_l}\right\}\right]\frac{1}{\delta_b} \\ &= -L\frac{1}{T}\frac{\Delta\mu(a \to c)}{\delta_b} \end{aligned} \tag{2.4.10}$$

Looking at the final equation one can predict three different outcomes for the oil droplet depending on which direction the forces works. Letting the osmotic force work in the positive direction, then depending on the interfacial tension the droplet can move both ways or stand completely still. If $\mu_w = -\mu_c$ there will be no movement. To do so the Interfacial tension between the water solution and octane needs to be lowered when adding the solute. This can very well happen and for most compounds it will actually be true, except the one with strong ionic forces. This one will contribute in a positive way to the osmotic force and increase the total force.

The final equation can also be compared with Fick's law $J = -D\frac{dc}{dx}$. This will be done to relate the results to a diffusion coefficient and thereby get a more practical view of the results. The relation between the diffusion coefficient and L is rather easy

$$L = \frac{DV_w}{R} \tag{2.4.11}$$

Where V_w is the concentration of pure water and D is the diffusion coefficient.

2.5 Calculations

The first and most important task is to find the transport mechanism of the water. Will the water diffuse through the oil phase or will it migrate along the wall of the tube? To distinguish the two mechanisms one needs to look at the determining variables for the speed of the oil droplet. Obviously the forces mentioned in the previous subsections are important, but they are after all constant for each system. This is not completely true because the concentrations will change with time, because of the water transport, and so will the osmotic gradient and interfacial tension. However, for the calculations they are assumed to be negligible. The movements can still differ from one capillary tube to another depending on size and material, and thereby lead to differences in the water flux. By comparing different capillary tube systems, it is possible to answer the questions stated in this project.

Another factor that is important for the transport, or the speed of the oil droplet, is the length of the oil droplet together with the area or circumference. If the mechanism is diffusional one have to look at the volume the water have to pass through, while if the migration is along the walls one need to look at the area of the wall. The oil droplet can be assumed to have the shape of a cylinder, and then the volume is proportional to the radius squared, while the area of the wall is just proportional to the radius.

Flux equations and transport mechanism

The water flux is expressed as the mole change per time unit, divided by an area. In this case we want to see if the migration of water is dependent on the cross sectional area of the capillary tube or just the circumference of it, I will come back to this. The equations below show an expressions for the water flux where A is an area. The two first ones are for each of the droplets, while the third is the total water flux, set to positive even though the two fluxes are in opposite directions.

$$J_w(a \to c) = \frac{1}{A}\frac{\Delta n_w^a}{\Delta t} \tag{2.5.1}$$

$$J_w(e \to c) = \frac{1}{A}\frac{\Delta n_w^e}{\Delta t} \tag{2.5.2}$$

$$J_w = \frac{1}{A\Delta t}(\Delta n_w^a + \Delta n_w^e) \tag{2.5.3}$$

In this case the A will be the cross sectional area of the capillary tube, πr^2. This expression can be set equal to the contributing forces earlier mentioned to get the whole picture of the system.

For a more practical point of view, one can express the water flux as a volume flow, and then relate it to the actually measured speed of the oil droplet.

$$J_v = J_w(a \to c)V_w + J_w(e \to c)V_w \tag{2.5.4}$$

Where J_v is the volume flux and V_w is molar volume. The dimensions of the volume flux will be $\frac{m^3}{m^2 s}$ or just m/s. This means that the volume flow is directly related to the speed of the droplet which again can be expressed as

$$J_v = \frac{\Delta V}{A\Delta t} = \frac{\Delta x}{\Delta t} = v_w^a + (-v_w^e) \tag{2.5.5}$$

Where Δx is the change in distance between the droplets, which corresponds to the sum of the movements of both droplets. The negative sign comes from the fact that the droplets are moving in the opposite direction. They will be separate water fluxes and they can be expressed as the equations bellow as earlier mentioned.

$$J_w(a \to c) = -L\frac{1}{T}\frac{\Delta\mu(a \to c)}{\delta_b} \tag{2.5.6}$$

$$J_w(e \to c) = -L\frac{1}{T}\frac{\Delta\mu(e \to c)}{\delta_d} \tag{2.5.7}$$

In this case the two differences in chemical potential will be the same, but in opposite directions. When adding the two fluxes together it will only be the thickness of the oil droplet that differs.

$$J_w(a \to c) + [-J_w(e \to c)] = -L\frac{1}{T}\left[\frac{\delta_b + \delta_d}{\delta_b\delta_d}\right]\Delta\mu(a \to c) \tag{2.5.8}$$

Instead of taking the average thickness over the two droplets one can be more precise and use the expression above for the thickness. The reason why I look at both the water fluxes together is that, in some way, there is a correlation between the movements of the two oil droplets. The distance between them is very small, so it is likely to think the movements can influence each other a little. All the measurements that are done will give directly a volume flux rather than the molar flux, for the molar fluxes I have assumed that it is 54,58 moles per liter of water at 60^o C.

The problem with this approach is that we look at the whole cross-sectional area of the tube no matter if the water transport is along the wall or diffusional, equation 2.5.5. In reality the area where there is a transport of water will be a lot smaller if the migration happens along the wall, Figure 2.5.1 illustrates the problem.

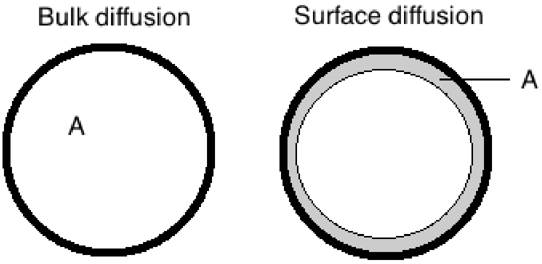

Figure 2.5.1: The effective diffusional area for the two transport mechanisms, cross sectional cut of the capillary tube

With this in mind it is obvious that looking at a plot of the water flux against the radius will make it difficult to draw any conclusion from. However, by looking at the amount of water passing from one side to another per time unit, $\dot{V}$, will be a lot better. This is easy to calculate and is not dependent on the radius of the tube in the same way as the water flux, Equation 2.5.9

$$\dot{V} = \pi r^2 \frac{\Delta x}{\Delta t} \tag{2.5.9}$$

By plotting this volume flow against the radius of the capillary tubes for systems with the same osmotic gradient, one should be able to distinguish if the flow is dependent on r or r^2 and thereby the two different transport mechanisms. Figure 2.5.2 shows an example of the plot with the two possibilities explained, with constant osmotic force. It can of course be a mix of the two as well or other possibilities. If the system had any surfactant it could have been very different again. It is important to mention that this assumes that the capillary force is negligible. If the capillary force contributes it will change the shape of the curve when it gets closer to zero.

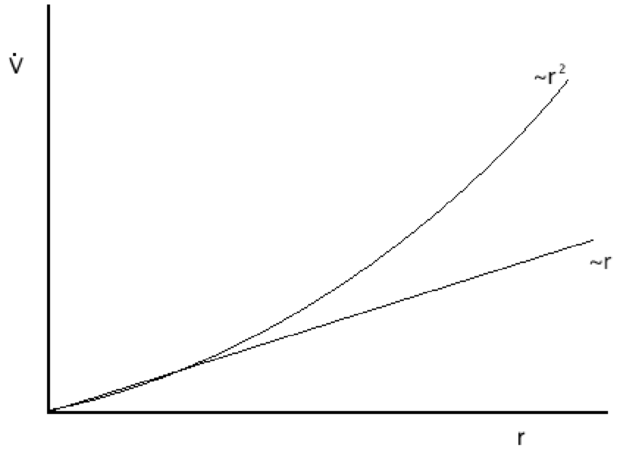

Figure 2.5.2: Example graph for the two different transport mechanisms for constant force

The capillary force

The influence of the capillary force is, as mentioned earlier, very hard to distinguish. However it is possible with some assumptions. First I will describe the case where the transport mechanism is along the walls. Then one can look at the problem as parasitic drag, which means the drag from a fluid that is passing at the surface of a solid, makes to the solid. In reality it will be the friction, or usually referred to as skin friction, when the water is moving from one side to another. Since the movements are so slow it is a fair assumption that the oil phase is also standing still. So this friction force that tries to stop the water, or pulls the wall/oil phase, should be proportional to the area of the surface it is passing.

$$F_f \propto A = 2\pi r\delta \tag{2.5.10}$$

Where F_f is the force caused by the friction and δ is the thickness of the oil droplet. If the radius of the tube is changed, the area will change according to the difference in radius, r. The area of the water flux which is illustrated in Figure 2.5.1, and can mathematically be expressed as in Equation 2.5.11. Where δ_r is the difference in radius from the inner to the outer circumference, and r is the outer radius. When the difference in radius becomes small, the curvature becomes negligible and it is getting closer to a rectangular area as in Figure 2.5.3.

$$A = \pi[r^2 - (r - \delta_r)^2] \tag{2.5.11}$$

If this assumption holds and δ_r does not change when the radius change, one can say that the change in water flux area when the tube size is changed is promotional to δr, like the friction.

Figure 2.5.3:

$$A = 2\pi\delta_r r \qquad\qquad \Delta A = 2\pi\delta_r\Delta r \tag{2.5.12}$$

Both the change in the skin friction area and the change in the water flux area are proportional to the change in radius. This means that the water flux will be constant no matter the size of the tube if the capillary forces does not contribute. This will be the case if the migration is along the walls and not a bulk diffusion. For the bulk diffusion it will be the same trend, but it is a lot easier to derivate. Here the water flux area will be the same as the diffusion area, which can be looked at as the resisting force. The length of the droplet is important for both the two resisting forces, but by multiplying the water flux with the length of the droplet one will have fluxes that are comparable with each other, see Equation 2.4.10. This last thing is done for all the results to be able to compare them.

3 Experimental

The experiments were done at an elevated temperature, 60 $^\circ C$, to speed up the process. Three different types of capillary tubes with different radius were used; 0,70 (Vitrex type 90/120), 0,26 (Blaubrand IntraMARK 10 μL) and 0,16 (Blaubrand IntraMARK 1-5 μL). To make a good temperature distribution the capillary tubes were put into glass vessels that where inside a larger water bath, and the bath itself had a continuous water flow around the vessels. In this way the water solution had homogenous temperature distribution. Each vessel was filled with sodium chloride solution (0,01M), and covered to avoid evaporation of water that could lead to change in sodium chloride concentration.

3.1 The solutions

Solutions with various salt concentrations were prepared in volumetric flask with the desired amount of sodium chloride. There were four different concentrations; 5.0M, 2.5M, 1M, 0.5M and a 0.01M for the bulk phase. The 0.01M solution was added to the large glass vessels and put into the water bath ready for the capillary tubes to be added. The reason doing this is, first of all, to be able to have a closed water bath where no water can evaporate from, and at the same time have a stable and homogenous temperature distribution. It is easier to cover a vessel rather than the whole water bath. Another very important reason is that having all the tubes in a vessel ables you move them under a microscope to see the movements more accurate. This turned out to be crucial for having successful measurements. Moving the tubes individually into a separate water bath for investigations was almost impossible do to without getting air bubbles into the tubes.

A tiny amount of fluorescein was added to the water (about 0,0010 g per 50 mL), which seemed to be more than the saturation limit, so the excess was removed. Then they were tested under UV-light to see the fluorescence effect, Figure 3.1.1. An interesting observation was that the dissolving limit seemed to be lower at high salt concentrations. Fluorescein was tried mixed with octane as well to see if it was soluble in both solutions, and thereby works as a surfactant. It did not seem to be soluble at all, and there was no fluorescence effect when exposed to UV-light, Figure 3.1.2. However, when it was solved in acetone, it gave a strong fluorescence effect, which indicates that the solute does not significantly effect the emission spectrum from the fluorescein, and it confirms that it was insoluble in octane.

3.2 Fluorecense effect

Octane is an organic substance which is rather colorless and therefor hard to visually separate from water. It is possible to distinguish the two substances in a capillary tube with the bare eye, but it is difficult especially for the very thin

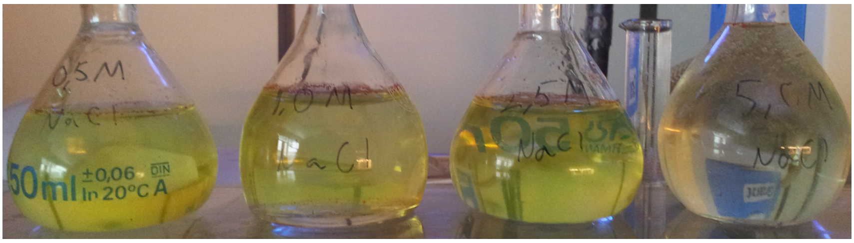

Figure 3.1.1: Four different sodium chloride solutions with an exceed about of fluorescein added

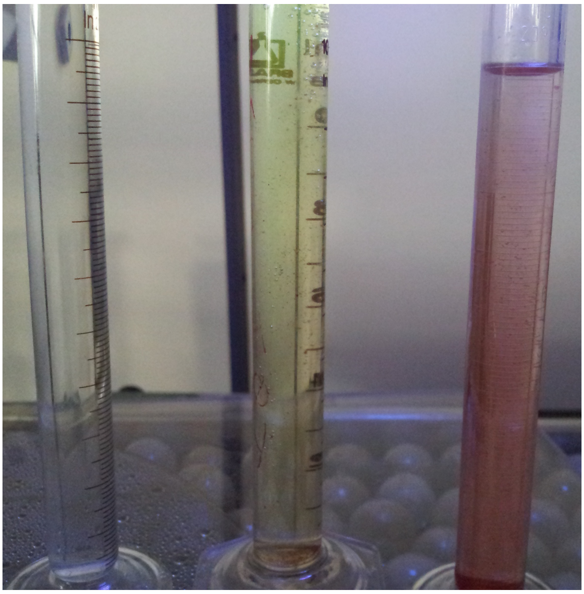

Figure 3.1.2: Three solutions. To the left distilled water, middle sodium chloride with fluorescein, to the right octane with fluorecein

tubes. This is very important for the measurements because they need to be very accurate due to the small movements.

Fluorescein can be used as color for the water phase. This is a widely used synthetic organic compound that has red crystals in its powder form. As mentioned earlier it is very important for the system to not have any surfactants because this will for sure lead to a micelle transportation of water and salt. Fluorescein has a very low solubility in water, but seems to be immiscible with octane. It is also a really strong color agent with a great fluorescence effect in UV-light. These two reasons make it perfect to use in this project, together with the fact that it is a very harmless substance that is actually used in medical diagnostics. The concentration of fluorescein needed is extremely low, and under strong UV-light it can be visible for concentrations down to *ppm*.

Fluorescence is a luminescence effect caused by excitation electrons and emission of photons. This means that there is a light source emitting but not as a result of heat, but so-called cold body radiation. A characteristic of fluorescence is that the absorbed photons have higher energy than the emitted ones. This is also the case for fluorescein which absorbs light with a maximum wavelength of about 490 *nm* while the emission wavelength will for this case have a maximum of about 510 *nm*. Note that these values change with different pH and solvent [16]. For this reason it is possible to use UV-light, that will be invisible for human eyes, to make the fluorescein radiate light in the visual spectra. This makes it easier to see the movement of the oil droplet.

To understand why the fluorescein emits photons of lower energy than it absorbs, one needs to look at quantum chemistry behind excitation and relaxation of electrons. Figure 3.2.1 shows an energy diagram for a very simple system with two possible ways for the electrons to go back to the initial state, fluorescence and phosphorescence. These two ways give more or less the same visual effect except that phosphorescence can be a lot slower and thereby the substance will glow even after it is exposed to light. However, the reason why the photons have less energy is because of the loss to vibrational energy before the electron relax to it's initial state. When the electron is not quantum mechanically allowed to directly relax to the initial state, it has to go through the intersystem crossing. In theory this is how the two effects are separated, but in practice it is just how fast the relaxation goes.

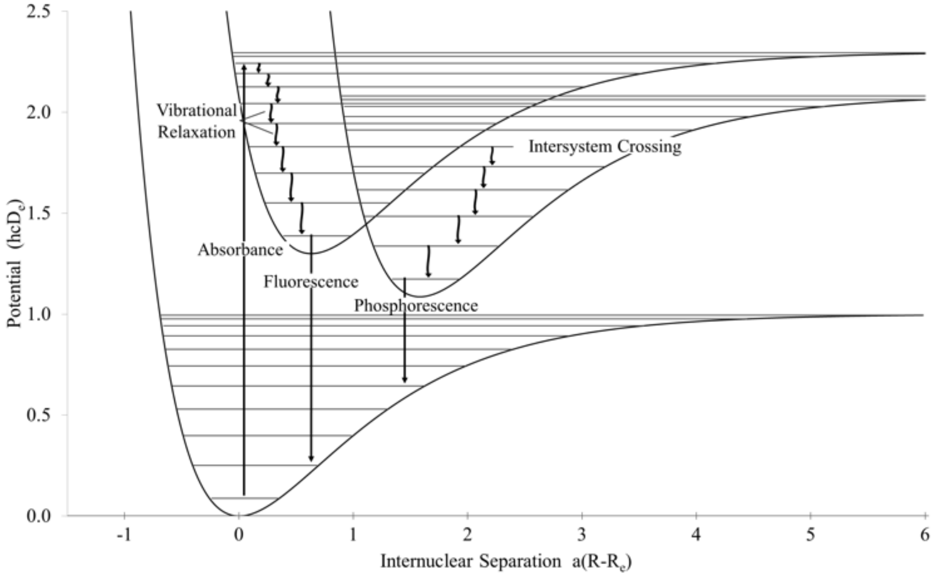

Figure 3.2.1: Energy diagram for excitation of electrons and the emission of photons either by fluorescence or phosphorescence [17]

3.3 Filling and measure the capillary tubes

The apparatus itself is rather simple, capillary tubes. However the way they are filled with different phases is more complicated. Figure 2.1.1 shows a sketch of the tube including the different phases. The challenge for this set up is to get all the phases into the capillary tube without having air bubbles. The air bubbles can come at the interfacial regions and then a change in the interfacial contact, or the bubbles can come in the water phases and block the diffusion of water and sodium chloride that needs to be there to keep a homogenous concentration.

The tubes were first filled by simply lowering them into the different solution in correct order, and controlling the amount of liquid that get in by covering the other end of the tube. The capillary force was not strong enough to fill the tube completely, so the last water phase was injected with a syringe. This means the tube was lowered into solutions in the following order: water bulk phase (just a little), oil phase, high salinity water phase, oil phase and water bulk phase again. The volume for each of the phases were controlled by how deep the tube were lowered. The end of the tube was turned and a syringe was moved into the small water bulk phase. By taking the syringe slowly out at the same time as releasing some water made it possible to avoid air bubbles.

The tubs were put into the glass vessel in the water bath. The whole process was done in two batches and it was always made three tubes with the same specifications, so that the results could be compared with each other and also in case something went wrong. Except for the very smallest tube in the first batch. Here two of the glass tubes had incorrect phase layers, one with three oil droplets and one with only a single. This was hard to visually observe when they were made, but a look in the microscope discovered it. The two tubes where removed.

3.4 Accuracy and uncertainty

All the measurements were done by looking at the tubes in a microscope and determining the change in position relative to a marker line. A ruler was put beside the tube as the reference. It is obvious that the uncertainty is rather high in the measurements where there are almost no change in position. However, it is very hard to determine a specific uncertainty for all the measurements. The results for volume flow and water flux are based on the average movement of the droplet over three measurements and the uncertainty is set to be the standard deviation of the three measurements. This excludes the uncertainty of the measurements, but the difference in the measurements are so high that it is covering all the other uncertainties.

The uncertainty in the radius is varying form 0,5 to 0,6% of the volume of the tube. Least mean-square method are used for estimating the uncertainty of the radius based on this.

4 Observations

During the experiments different problems have been popping up, and the first was caused by various methods of filling the tubes. The injection worked well for the largest tubes, but the syringe was too big for the smaller ones. The capillary force have been of great help, but it was not enough to fill the tubes. Most of the times there was a little room left in the tube. Also it was observed that it was particularly difficult to get the second oil phase into the tube, if the tube was filled a little too much it was impossible with the use of the capillary force, which was the only possibility found.

For the small tubes it was only one option, to fill them as much as possible and put them into the solution and then break them. Two tweezers were used to break the tubes. This gave a better and more precise breaking point rather than using hands. The problem with breaking the tube is that the droplets usually moves a little bit in the breaking process, and after they are put into the water bath it is not possible to make any lines on the tube with a marker. However, by looking in the microscope and measure the movement, one can compensate for the error.

The fluorescein effect was smaller than expected, and thereby not a big success. It was visible in the small tubes, but it requires very dark environment. Unfortunately my laboratory had large windows and the process of moving the tubes into a different room, together with the microscope, was not very good solution.

The accuracy of the measurements can always be questioned when the movements are so small. It was also the case for this project. All measurements were done just by looking at the tubes in a microscope together with a ruler. I am sure this can be further improved with a digital optical light microscope that can take pictures. Comparing the pictures from each measurement, can hopefully give better results. For the tubes with small movements it was crucial to know where on the marker line the measurements where done. A line with a normal thin marker would have a width of about $0,2 - 0,4mm$, depending on if it is straight or not, and that is more than the movement of the droplet.

Another factor that influence the accuracy is the formation of gas bubbles in the tube. The tubes in the first batch was filled with room tempered octane and water solutions. This caused a problem because they were heated to 60^oC and thereby a big change in vapor pressure that lead to formation of small bubbles. As long as the bubbles do not block the whole tube, there should be no problem for the movement. But the bubbles will make the droplet larger. This will effect the movement depending on which direction the droplet expand. Luckily in this project it was measured both sides of the droplet so it was possible to take into account the change in size when measuring the movement, but I chose not to change thickness of the droplet, δ_i, when calculating the fluxes.

5 Results

All the measurements that have been done are included in Appendix B, while the tabulated data for the calculations are in Appendix C. This includes all the experimental data that have been used for the plots in this section. The results presented will be commented here, and further discussed in the next section. A very important result of this project is the water flux equation already presented in the theory.

$$J_a = -L\frac{1}{T}\left[RT\ln\left(\frac{P_{2,vap}}{P_{1,vap}}\right) + 2V_o\left(\frac{\gamma_{w,h}\cos(\theta_h)}{r_h} - \frac{\gamma_{w,l}\cos(\theta_l)}{r_l}\right)\right]\frac{1}{\delta_b}$$

This clearly shows all the known forces contributing to the migration of water in the capillary tubes. All the variables are in principle measurable, but the interfacial tension as a function of salt concentration is expensive and difficult to measure.

5.1 Chemical potential

The chemical potential differences over the droplets were calculated from the differences in vapor pressure according to Equation 2.2.3, and are presented in Table 5.1.1.

Table 5.1.1: Tabulated values of the difference in chemical potential for various sodium chloride concentrations against a 0,01M solution, at 60^oC

c_2 to c_2 $[mol/L]$	$P_{vap,2}$ $[kPa]$	P_{vap} for 0,01M $[kPa]$	$\Delta\mu$ $[kJ/mol]$
5,0 to 0,01	11,13	19,96	1,62
2,5 to 0,01	15,12	19,96	0,77
1,0 to 0,01	17,91	19,96	0,30
0,5 to 0,01	18,90	19,96	0,15

5.2 Capillary force

The contribution from the capillary force can be estimated from equation 2.4.7. The problem is that there are many unknown variables in this equation. The interfacial tension is not known for the different sodium chloride concentrations, and neither is the contact angle. The radius of the meniscus will be the same as the tube radius if the contact angle is 0, and later is very often assumed for pure water against glass. The change in interfacial tension for pure water have previously been discussed and the change is rather large at high salt concentrations. Figure 5.2.1 shows a plot of the capillary force as a function of the radius of the meniscus with the following conditions and assumptions:

- 25^oC and 1 bar

- The contact angles are the same for both solutions
- The change in interfacial tension is set to be 5 mN/m (like it is for pure water against 2,7M)
- The radius can be assumed to be the same as the tube radius

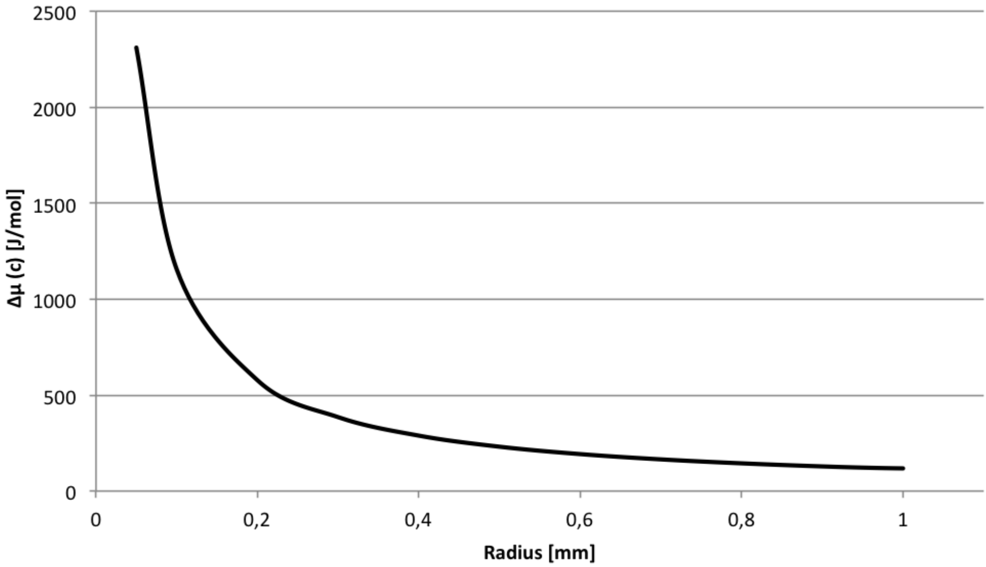

Figure 5.2.1: Simulated values for the capillary force as a function of the radius of the meniscus in the system under the conditions mentioned in the text.

As expected there is a large raise in the capillary force when the radius is getting smaller. The values are very well comparable to the one for the osmotic force, and for the small radiuses it is clear that the capillary force can influence. The assumptions and conditions are very realistic as well.

5.3 Movement of the oil droplet

The measurements that have been taken clearly tell us that there is a movement of the oil droplets in the systems, and it is because of the osmotic gradient. By changing the concentrations of the sodium chloride solutions it is clear that it effects the speed of the droplet. Figure 5.3.1 shows a plot of the water flux (over area A) against the difference in chemical potential. Note that the capillary force is not included in the chemical potential term, because it is not known for the different solutions. If the capillary force has a significant impact on the system it will contribute to the slope of the curve of this plot.

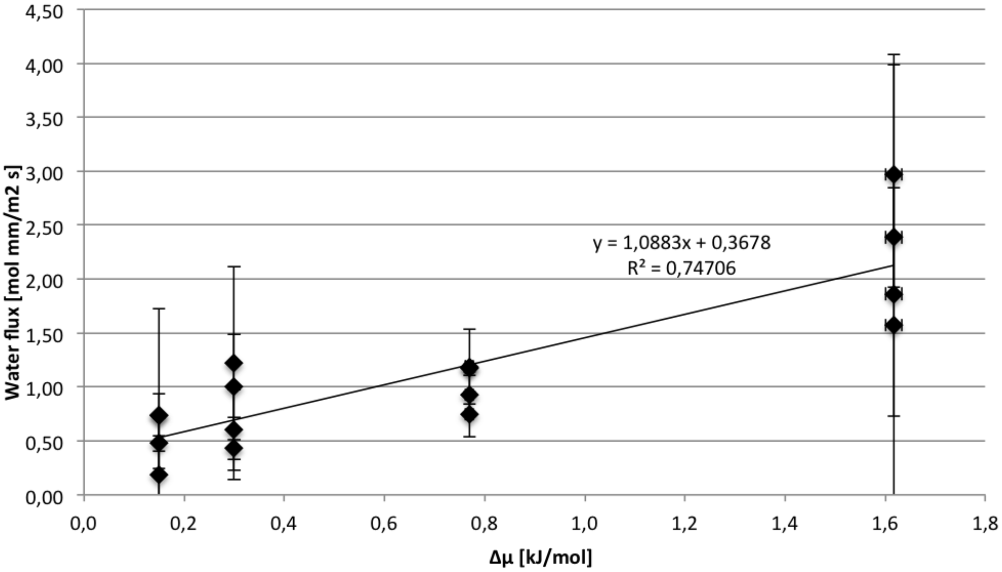

Figure 5.3.1: Plot of the volume flux of water against the difference in chemical potential for various of sodium chloride solutions

The ideal situation would be if the intersection point was through the origin. By forcing the trend line to pass through the origin will give a slope of 1,40, but the R^2 value will be 0,64. However this slope can be used for calculating the constant L with the dimensions $\frac{mol^2 sK}{kgm^3}$. With some dimension changes and calculations I was able to find $L = (1.26 \pm 0.11) \cdot 10^{-11} \frac{mol^2 sK}{kgm^3}$ for the linear regression in Figure 5.3.1 and $L = (1.62 \pm 0.14) \cdot 10^{-11} \frac{mol^2 sK}{kgm^3}$ if the line is forced through the origin.

Relating the L to the diffusion coefficient in Fick's law with the relation from Equation 2.4.11 gives the diffusion coefficients $D = (1.08 \pm 0.10) \cdot 10^{-7} \frac{m^2}{s}$ for the regression that is forced through the origin.

5.4 Transport mechanism

The main goal of the project was to find the transport mechanism. Figure 5.4.1 shows a plot of the volume flow versus the radius of the tube with including error bars.

A regression of the plot indicates that a polynomial trendline is slightly better than a linear. However the difference is so small that I do not want to include the regression curves as a result. The plot might not look as expected because it is confirmed that the capillary force is significant at for the smallest tubes.

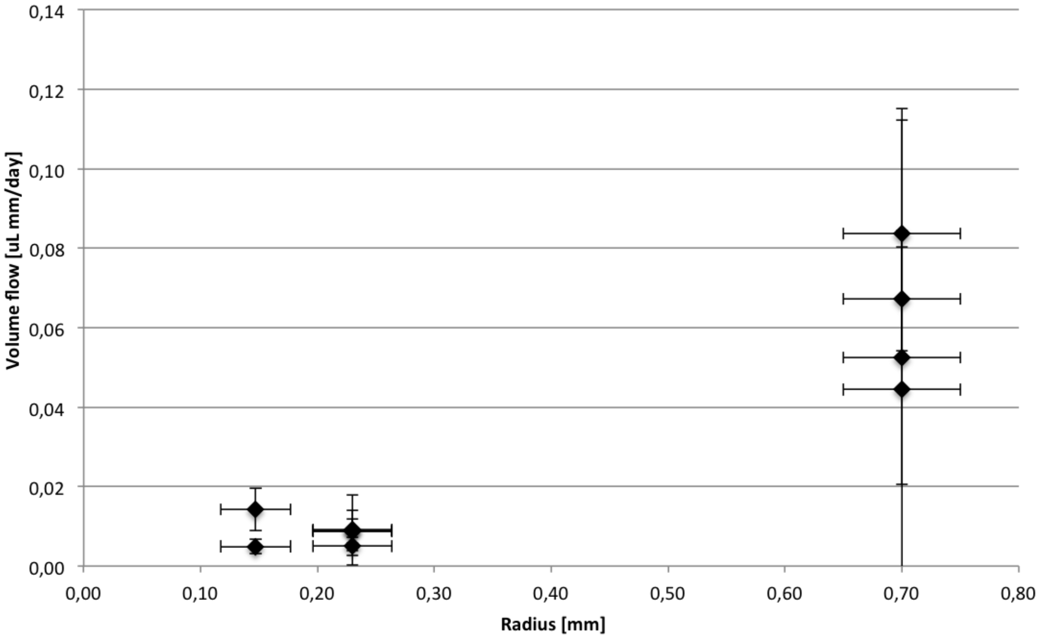

Figure 5.4.1: Plot of volume flow versus the radius for the system including error bars.

5.5 Distinguishing the two forces

To two contributing forces for the movement of the droplet are osmotic gradient and capillary force. From the experiments done it is unfortunately impossible to distinguish these two forces directly. However, as mention in the theory it can be done with some assumptions. A plot of the water flow against the radius of the tube should give a straight line with a slope equal 0 if the capillary force does not contribute. When or if the capillary force is large enough the line will change, most likely when the radius of the tube gets very small. Figure 5.2.1 shows the expected situation for simulated data. Figure 5.5.1 is the plot of the experimental values for this project.

This plot shows a similar behavior as the one for the calculated values, but the increase seems to come at even lower radiuses. This can very well be true, because the calculated data are based on some assumptions. It is good that the two plots have similarities, and with more experiments it could be possible to give estimates for the change in interfacial tension and contact angle, which again will decide the radius of the meniscus. A plot of the theoretical total force, the capillary force and the osmotic force together, against the radius is shown in Figure 5.5.2. This to give a better comparison to the experimental plot where both forces are included.

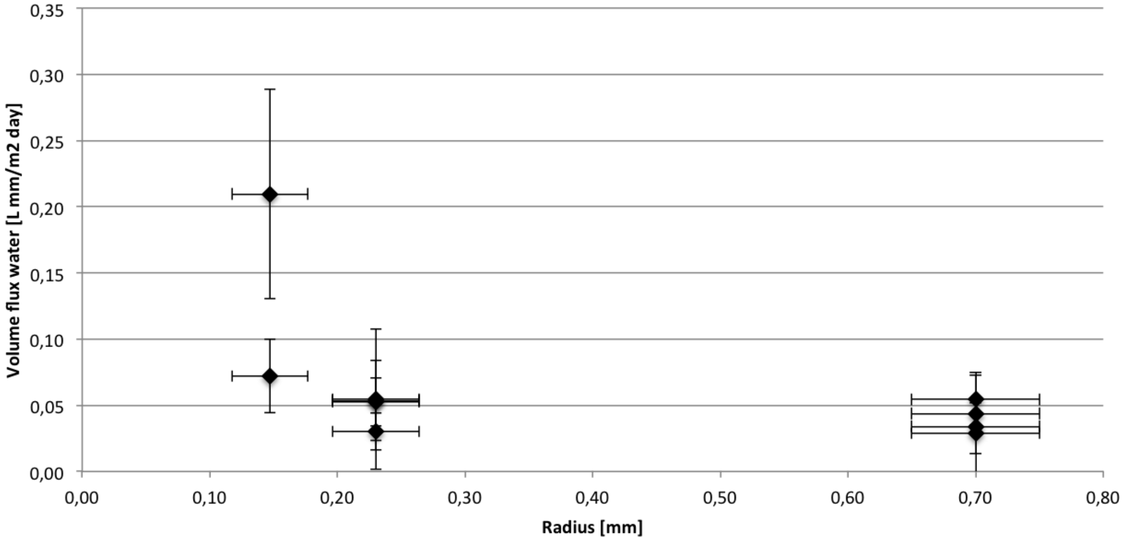

Figure 5.5.1: Plot of the water flow against the radius of the tube for the experiments

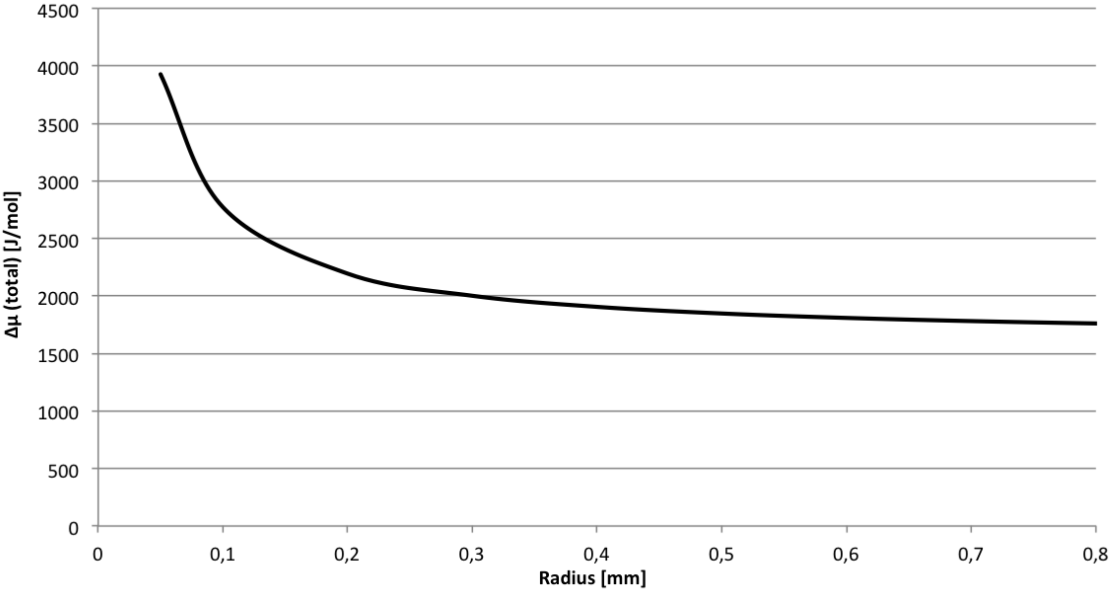

Figure 5.5.2: Plot of the total estimated force against the radius of the meniscus, with the assumptions mention earlier.

6 Discussion

This project has had many ups and downs and it is quite hard to find good solutions for all the problems. There were three main questions to start out with, and I have tried to answer them as good as possible. Sometimes it is not necessarily the result that makes the project good, but the knowledge of the mistakes and how to improve the results. This is very important, and at least if one look at the accuracy of the measurements done. At first it almost looked like a cloud of points, impossible to make any regression or understand in any way, but that was of course and luckily, before I put in the correct formulas in excel.

6.1 Theoretical estimates

The two forces were theoretically calculated and the results were presented. The osmotic force was calculated based on values for osmotic coefficient found by Gibbard et al. [9], and are not really theoretically calculated, because they are based on experiments. However, they are based on the assumption that the change in activity is equal the ratio of the vapor pressure, which is a pretty common assumption. These values are for sure realistic and also used in the plots of the experimental data.

The estimation of the capillary force is a little more vague. The conditions were explained in the results and I would like to verify them here.

- The first assumption is the temperature, which is 25 degrees celsius. It is known that the capillary force is lower at higher temperatures, so the values can be adjusted a little if one was to compare it directly with the experiments.

- The second assumption that the contact angle is the same for both sodium chloride concentrations is of course not completely true. The value of cosine to an angle close to 0 does not change very much. From 0 to 10 degrees it changes from 1 to 0.985, which is nothing compared to a small change in some of the other variables. Knowing that pure water has a contact angle of 0, makes this assumption quite reasonable.

- The third assumption was that the change in interfacial potential is about 5 mN/mol is maybe the most questionable one. The change in interfacial tension of pure water to a 2,7M water solution is about 5 mN/mol [13] and the change is linear with the concentration up to this value. If the trend continues over 2,7M, a change from 0,01M to 5,0M should give raise to an even larger change in surface tension. However, I do not know if the change can apply for the interfacial tension. But looking at the estimates from Fawkes equation 2.3.3 one can see that the interfacial tension seems to relate to the special interacting forces and not the dispersion forces. The special interacting forces for water are hydrogen bondings, which are highly polar bonds that the sodium chloride ions will interact with. Then since the surface tension of water increases with salt concentration it is likely to think that the interfacial tension does the same. I have chosen to only increase it with 5 mN/mol, because I do not know weather the trend continues or not, so this should be on the safe side and cover for the assumptions. A larger change will of course lead to an even larger effect from the capillary force, but it will not change the shape of the curve and thereby not the point where it starts to increase faster.

- The fourth is not really an assumption, but it just makes it easier to compare with the results if the statement is true. It also correlates with the assumption that the contact angle is close to zero.

The result of the plot is very interesting and it shows that the capillary force is expected to contribute significantly at a radius lower than 0,2 mm. Although there are some uncertainties involved, it still gives a quite realistic value as a start out point. The smallest tube used in the experimental part of this project is 0,15 mm, so one should expect the water flux of these tubes to be a littler higher.

6.2 Does the osmotic gradient effect the oil movement?

It is evident that the chemical potential difference is the reason for the movement of the oil droplet. The plot in Figure 5.3.1 has a quite good linear regression fit, with a slope that can correspond to the phenomenological coefficient, L. From the results it does not look like the capillary force has any significant impact of the water migration for the larges tubes, which are used for this plot. This is important to know because the capillary force was not part of the variables in the plot and therefor it would be participating in the slope of the curve.

There is one mysterious part of this plot, and that is the intersection point. Mathematically this means that there will be movements of the oil droplets even without any concentration differences. However, I cannot see any other forces that would contribute to the movement, and it might just be my eager to see a change when I measured the movements. After all the movements were very close to zero, and it is difficult to measure the changes very accurate. A change on 1 mm could give quite a big impact on the results. This is something that very well can be improved by letting the tubes stay longer or increase the temperature of the water bath. The first option will for sure give longer distances, while the second is not completely sure.

The diffusion coefficient was reported, and it is reasonable compared with what Schatzberg reported [18]. They reported diffusion coefficient to be $5,97 \cdot 10^{-5} \frac{cm^2}{s}$ for $45^o C$ for n-hexadacane, which is about 20 times smaller than the reported result in this report (note the difference in dimensions). If the results from Schatzberg are extrapolated to $60^o C$ assuming a linear trend (R^2 value of 0,99), it will give $9,03 \cdot 10^{-5} \frac{cm^2}{s}$, and is only about 10 times smaller. It is likely to think that the smaller octane molecules can transport water molecules faster and thereby have a higher diffusion coefficient. Water has also a higher solubility in octane than hexadacane. This makes the result trustworthy and diffusion can be a very realistic transport mechanism for the water.

6.3 What is the mechanism for the water migration?

This was set as the main question for the whole project, and the results are yet not very clear. The experiments are very narrow and only look at completely circular tubes made of glass. It will be very different in a real oil reservoir where the walls are made of porous stone and not at all circular. If the walls are more hydrophobic maybe it will favor a bulk diffusion. On the other side, if the walls have various shapes and are hydrophilic it will for sure favor migration along the walls but will it open for transfer of sodium chloride ions as well? Figure 6.3.1 shows the cross section of two possible pore shapes, not suppose to illustrate real situation, but just as examples. A system always wants to be in the lowest energy state, and if the oil is not attracted to the walls it will want to form spheres to reduce the total surface tension. That is why it will not fill all the corners on the sketch. This shape will leave cavities for the water to migrate, and if they are big enough it would be possible to transport ions as well.

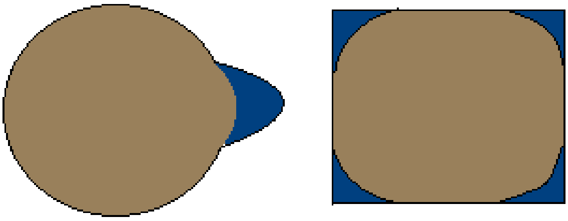

Figure 6.3.1: Example of the cross section of two possible pore shapes

The results of this project are difficult to draw any conclusion from. It is only three different radiuses and two of them are too close to each other. It would have been desirable to have more variation in size and more measurements, but this was the equipment given and I actually thought it would be enough. However, during a 4 months project it is hard to know what the outcome will be, when each experiment takes about 40 days. It would defiantly have been interesting to have a point in-between the radius of 0,23 and 0,70, and maybe a point larger than 0,70. This could perhaps have been sufficient for drawing a conclusion, but the inaccuracy would still have been a big problem.

A linear regression gives a R^2 value of 0,86 while a second degree polynomial regression gives 0,88. However, by looking at the curve it seems like the polynomial fits better for the low values. This might be because one of the points for the smaller radius is very high, and a polynomial fit allows the trendline to have a minimum and then increase again. Removing this point does not help either. Then both the regressions have 0,88 in R^2 value. One also needs to keep in mind that the points for the smallest radius in reality are not relevant because the capillary force will contribute and change the shape of the curve.

6.4 Will the capillary force contribute?

The theoretical estimations tells us that the capillary force should contribute for the smallest tubes size. From the plot in Figure 5.5.1 one can see that the water flux increases slightly for the smallest tube and thereby it verifies the estimations done. The size of the increase is not possible to say something about. However, these results have some assumptions and there are only two points from the smallest tube and both with quite high uncertainty. One of the points seems to be way higher than expected and might not be very reliable, and one point is not much to draw conclusions from for these experiments. I have previously discussed how high the uncertainty of the measurements can be, however it decreases with increasing concentration difference. But this is only the uncertainty related to the actually measurements. However, all the fluxes are based on the average flux over three measurements, and the standard deviation of the average (the one used in the plots) is in many cases as high as the numerical value for the water flux. I would not have counted my life on these results, but they indicates that the capillary force can very well contribute.

A very good way to improve the results for this experiments will be first of all to change the walls of the capillary tube and see the effect on the speed. This can, as mentioned earlier, change the transport mechanism because water will attract more/less to the walls. That is why another solution might be even better. This is to plot the water flux against the differences in chemical potential like Figure 5.3.1, and for various of tube sizes. Then compare the slope of the curves, meaning the L value, for the different plots. If the L is dependent on the radius of the tube, then it will be clear that the capillary force contributes, if not the opposite of course. If the measurements are done for a large variety of tube sizes one can plot the L against the radius and see at witch radius the capillary force starts to contribute significantly. The plot will hopefully give a straight line for the large radiuses and then starts to change when the radius is getting lower.

7 Conclusion

The transport mechanism of water from one side of the oil droplet to the other, was the first problem to solve in this project. The experimental diffusion coefficient is in the same order of magnitude as expected for bulk diffusion coefficient. However, no such estimations were possible to do for the surface diffusion, so it can very well fit for this transport mechanism as well. The conclusion is that the water migrates because of the concentration difference of sodium chloride, and the experiments can confirm that a bulk diffusion can be the mechanism, but one cannot exclude the possibility of a surface diffusion along the walls.

The capillary force was estimated with some assumptions, and the experimental results confirmed a similar trend. It seems like the capillary force starts to significantly contribute to the water migration, when the radius of the tube is smaller than 0,20 mm. This means that if the tube radius is larger than 0,20 mm, then the movement is controlled by the difference in chemical potential.

8 Nomenclature

Symbol	Dimension	Description
a_i	$-$	Activity of component i in solution
A	m^2	Area (of the flux)
c	mol/L	Concentration
δ	m	Width of the oil droplet
δ_r	m	Difference in radius
J_i	mol/m^2s	Molar flux of component i
J_v	m^3/m^2s	Volume flux of water
F_c	N	Capillary force
G	J/mol	Gibbs' energy
G_i^o	J/mol	Gibbs' standard energy for component i
Γ_i	mol/m^2	Surface excess for component i
γ_i	mN/m	Surface tension for component i
γ^{disp}	mN/m	Surface tension caused by dispersion forces
γ^{sp}	mN/m	Surface tension caused by spacial interactions
λ_i	$-$	Activity coefficient for component i
L_{ij}	$-$	Phenomenological coefficient
m	mol/kg	Molality
μ_i	J/mol	Chemical potential for component i
μ_i^o	J/mol	Chemical potential for a pure component i
n_i	mol	Amount of substance i
O	m	Three phase contact line
P_i	Pa	Pressure
P_i^o	Pa	Pressure for reference conditions
P_{vap}	Pa	Vaporization pressure
R	$J/molK$	Universial gas constant
r	m	Radius of he meniscus
ρ	g/mL	Density
S_{irr}	$J/Kmol$	Irreverisble entropy production
σ_i	$J/Kmolm$	Local entropy production
T	K	Temperature
t	day	Time
θ	^{o}	Contact angle
V_i	L/mol	Molarity for the pure component i
$\dot{V}$	L/s	Volume flow
v_w	m/day	Speed of the droplet
x_i	$-$	Mol fraction
Δx	m	Change in position of the oil droplet

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A Calculations of vapor pressure of water at 60^oC

The data found were the osmotic coefficients at different molalities at 60^oC. This needs to be calculated to vapor pressure for different molarities. First by finding the relationship between molalities and molarities at 60^oC [10]. The tabulated data is listed in Table A.0.1 and a plot can be seen in Figure A.0.1

Table A.0.1: Tabulated values of molality and density.

$m[mol/kg]$	$\rho[g/mL]$
0,09842	0,9834
0,19683	0,9876
0,49160	1,0029
0,98320	1,0224
1,96300	1,0588
3,92200	1,1295

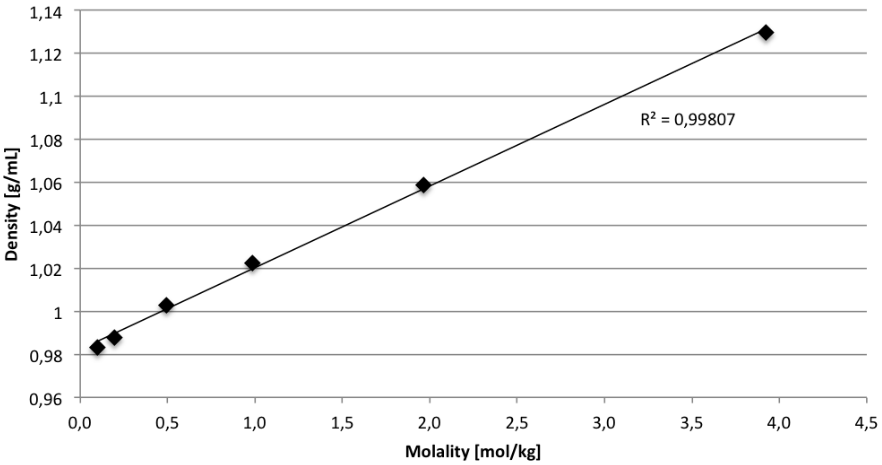

Figure A.0.1: Plot of density versus molality at 60^oC

The regression gives the following relation, where ρ is the density in g/mL and m is the molality in mol/kg

$$\rho = 0,038m + 0,9823 \tag{A.0.1}$$

The molarity was calculated and can be found together with the osmotic coefficients in Table A.0.2. The osmotic coefficient for 60^oC was estimated by interpolation between the values for 50^oC and 75^oC. The vapor pressures were calculated from the estimated values and plotted against the concentration in Figure 2.2.1. The tabulated values are given in Table A.0.3.

Table A.0.2: Tabulated values for osmotic coefficient for different temperatures and concentrations.

$m[mol/kgl]$	$c[mol/L]$	$T = 323,15K$	$T = 348,15K$	Estimated $T = 333,15K$
0,10	0,10	0,9317	0,9281	0,9303
0,20	0,20	0,9235	0,9198	0,9220
0,30	0,30	0,9214	0,9179	0,9200
0,40	0,40	0,9219	0,9185	0,9205
0,50	0,50	0,9237	0,9206	0,9225
0,60	0,60	0,9264	0,9236	0,9253
0,70	0,71	0,9297	0,9271	0,9287
0,80	0,81	0,9335	0,9311	0,9325
0,90	0,91	0,9376	0,9354	0,9367
1,00	1,02	0,9419	0,9399	0,9411
1,20	1,23	0,9513	0,9496	0,9506
1,40	1,45	0,9614	0,9598	0,9608
1,50	1,56	0,9666	0,9652	0,9660
1,60	1,67	0,9720	0,9706	0,9714
1,80	1,89	0,9831	0,9816	0,9825
2,00	2,12	0,9946	0,9930	0,9940
2,50	2,69	1,0249	1,0226	1,0240
3,00	3,29	1,0567	1,0533	1,0553
3,50	3,90	1,0898	1,0847	1,0878
4,00	4,54	1,1238	1,1166	1,1209
4,50	5,19	1,1583	1,1484	1,1543
5,00	5,86	1,1932	1,1800	1,1879
5,50	6,55	1,2282	1,2110	1,2213
6,00	7,26	1,2631	1,2410	1,2543

Table A.0.3: Tabulated values for vapor pressure for sodium chloride solutions at different concentrations, 60^oC.

$c[mol/L]$	Vapor pressure $[kPa]$
0,10	19,7
0,20	19,5
0,30	19,3
0,40	19,1
0,50	18,9
0,60	18,7
0,71	18,5
0,81	18,3
0,92	18,1
1,02	17,9
1,23	17,5
1,45	17,0
1,56	16,8
1,67	16,6
1,89	16,2
2,12	15,8
2,69	14,8
3,29	13,8
3,90	12,8
4,54	11,8
5,19	10,9
5,86	9,95
6,55	9,09
7,26	8,27

B Measurements

The experiments were done in two different batches. For each of the batches there was in total 18 capillary tubes, six different systems and three of each. For the first batch the movement of the droplet was measured after 18, 27 and 42 days, while the second was only measured after 13 days. All the measurements can be viewed in Table B.0.4.

Table B.0.4: Tabulated values of the movements for batch one and two.* measurement was done after 27 days

Tube id	Δx in 18 days [mm]	Δx in 9 days [mm]	Δx in 15 days [mm]	Δx in 13 days [mm]
5M #1	1,33	-0,15	0,48	-
5M #2	0,90	0,20	0,65	-
5M #3	1,05	0,15	0,45	-
5M #4	-	-	-	0,30
5M #5	-	-	-	0,40
5M #6	-	-	-	0,30
2,5M #1	0,38	0,20	0,33	-
2,5M #2	0,20	0,18	0,28	-
2,5M #3	-	0,33	0,28	-
2,5M #4	-	-	-	0,15
2,5M #5	-	-	-	0,10
2,5M #6	-	-	-	0,10
1,0M #1	0,53	0,08	0,15	-
1,0M #2	0,28	0,03	0,15	-
1,0M #3	0,15	0,13	0,05	-
1,0M #4	-	-	-	0,10
1,0M #5	-	-	-	0,10
1,0M #6	-	-	-	0,15
0,5M #1	0,00	0,03	0,13	-
0,5M #2	0,25	0,08	0,15	-
0,5M #3	0,18	0,18	-0,05	-
0,5M #4	-	-	-	0,10
0,5M #5	-	-	-	0,05
0,5M #6	-	-	-	0,15
5uL #1	2,30	0,83	3,43	
5uL #2	-	-	-	1,05
5uL #3	-	-	-	0,55
5uL #4	-	-	-	0,65
10uL #1	0,80	0,15	0,70	-
10uL #2	1,30	1,05	0,93	-
10uL #3	1,38	0,18	0,98	-
10uL #4	-	-	-	0,20
10uL #5	-	-	-	0,50
10uL #6	-	-	-	0,60

The corresponding thicknesses of the droplets can be seen in Table B.0.5.

Table B.0.5: Tabulated values of the thicknesses of the droplets for all systems, together with the average

Tube id	δ_1, left droplet [mm]	δ_2, right droplet [mm]	Average δ [mm]
5M #1	2,8	1,5	2,2
5M #2	4,8	2,0	3,4
5M #3	1,9	2,0	2,0
5M #4	2,9	4,0	3,5
5M #5	4,6	2,8	3,7
5M #6	4,0	2,9	3,5
2,5M #1	2,0	2,0	2,0
2,5M #2	1,9	1,5	1,7
2,5M #3	2,2	4,1	3,2
2,5M #4	3,8	3,3	3,6
2,5M #5	3,0	4,6	3,8
2,5M #6	3,2	6,7	5,0
1,0M #1	3,1	2,6	2,9
1,0M #2	1,6	1,8	1,7
1,0M #3	2,4	2,8	2,6
1,0M #4	4,6	5,7	5,2
1,0M #5	4,0	1,6	2,8
1,0M #6	3,5	6,7	5,1
0,5M #1	1,8	1,9	1,9
0,5M #2	2,8	2,3	2,6
0,5M #3	3,8	2,7	3,3
0,5M #4	5,4	1,2	3,3
0,5M #5	5,5	1,8	3,7
0,5M #6	2,3	2,4	2,4
5uL #1	3,2	1,4	2,3
5uL #2	2,2	0,9	1,6
5uL #3	3,0	2,8	2,9
5uL #4	4,2	4,1	4,2
10uL #1	2,1	1,4	1,8
10uL #2	1,7	1,0	1,4
10uL #3	3,0	1,5	2,3
10uL #4	3,7	1,6	2,7
10uL #5	4,6	1,0	2,8
10uL #6	6,7	4,0	5,4

C Tabulated values for the calculations

The calculated water fluxes can be observed in Table C.0.6. Note that these values are volume flow per area and thereby dependent on the area of the tube.

Table C.0.6: Tabulated data for the water flux for the different measurements, all at 60^oC. The A is the cross sectional area of the tubes. *Average is taken over three measurements

Tube id	First meas. J_w [$mol\ mm\ m^{-2}day^{-1}$]	Second J_w [$mol\ mm\ m^{-2}day^{-1}$]	Third J_w [$mol\ mm\ m^{-2}day^{-1}$]	Avg. J_w [$mol\ mm\ m^{-2}day^{-1}$]	STDEV [$mol\ mm\ m^{-2}day^{-1}$]
5M #1	3,9	-0,9	1,7	1,6	2,4
5M #2	3,8	1,7	3,3	3,0	1,1
5M #3	3,1	0,9	1,6	1,9	1,1
5M #4	2,1	-	-		
5M #5	2,9	-	-	2,4*	0,5
5M #6	2,1	-	-		
2,5M #1	1,14	1,2	1,2	1,2	0,04
2,5M #2	0,5	0,9	0,8	0,7	0,2
2,5M #3	-	0,9	1,4	1,2	0,3
2,5M #4	1,11	-	-		
2,5M #5	0,76	-	-	0,93 *	0,18
2,5M #6	0,91	-	-		
1,0M #1	2,3	0,6	0,8	1,2	0,9
1,0M #2	0,7	0,1	0,4	0,4	0,3
1,0M #3	0,6	1,0	0,2	0,6	0,4
1,0M #4	1,1	-	-		
1,0M #5	0,5	-	-	1,0*	0,5
1,0M #6	1,5	-	-		
0,5M #1	0,0	0,1	0,4	0,2	0,2
0,5M #2	1,0	0,6	0,7	0,7	0,2
0,5M #3	0,8	1,7	-0,3	0,7	1,0
0,5M #4	0,4	-	-		
0,5M #5	0,3	-	-	0,5*	0,2
0,5M #6	0,7	-	-		
$5\mu L$ #1	6,8	15	12	11,4	4,3
$5\mu L$ #2	2,8	-	-		
$5\mu L$ #3	3,4	-	-	3,9*	1,5
$5\mu L$ #4	5,7	-	-		
$10\mu L$ #1	2,0	0,8	2,1	1,6	0,8
$10\mu L$ #2	2,5	4,0	2,1	2,9	1,0
$10\mu L$ #3	4,2	1,1	3,5	2,9	1,6
$10\mu L$ #4	0,9	-	-		
$10\mu L$ #5	1,7	-	-	3,0*	2,9
$10\mu L$ #6	6,3	-	-		

Table C.0.7 shows the calculated volume flow, in this case meaning the volume of water per day in total, not just over a specific area.

Table C.0.7: Tabulated data for the volume flow of water for the different measurements, all at 60^oC. *Average is taken over three measurements

Tube id	Volum flow 1 [μLm/day]	Volum flow 1 [μLm/day]	Volum flow 1 [μLm/day]	Avg. volume flow [μLm/day]	STDEV [μLm/day]
5M #1	0,24	-0,06	0,10	0,10	0,15
5M #2	0,26	0,12	0,23	0,20	0,08
5M #3	0,18	0,05	0,09	0,11	0,06
5M #4	0,12	-	-		
5M #5	0,18	-	-	0,14*	0,03
5M #6	0,12	-	-		
2,5M #1	0,06	0,07	0,07	0,066	0,002
2,5M #2	0,03	0,05	0,05	0,043	0,012
2,5M #3	-	0,06	0,09	0,07	0,02
2,5M #4	0,06	-	-		
2,5M #5	0,04	-	-	0,055*	0,009
2,5M #6	0,06	-	-		
1,0M #1	0,13	0,04	0,04	0,07	0,05
1,0M #2	0,04	0,01	0,03	0,025	0,016
1,0M #3	0,03	0,06	0,01	0,03	0,02
1,0M #4	0,06	-	-		
1,0M #5	0,03	-	-	0,06*	0,03
1,0M #6	0,09	-	-		
0,5M #1	0,00	0,01	0,02	0,011	0,012
0,5M #2	0,05	0,03	0,04	0,042	0,011
0,5M #3	0,05	0,10	-0,02	0,04	0,06
0,5M #4	0,04	-	-		
0,5M #5	0,02	-	-	0,034*	0,011
0,5M #6	0,04	-	-		
$5\mu L$ #1	0,020	0,045	0,036	0,0337	0,013
$5\mu L$ #2	0,008	-	-		
$5\mu L$ #3	0,008	-	-	0,010*	0,003
$5\mu L$ #4	0,014	-	-		
$10\mu L$ #1	0,013	0,005	0,014	0,010	0,005
$10\mu L$ #2	0,016	0,026	0,014	0,019	0,007
$10\mu L$ #3	0,029	0,007	0,024	0,020	0,011
$10\mu L$ #4	0,007	-	-		
$10\mu L$ #5	0,018	-	-	0,022*	0,018
$10\mu L$ #6	0,041	-	-		