FLOW OF DILUTE EMULSIONS THROUGH POROUS MEDIA

PROEFSCHRIFT

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Chapter 1

Introduction

1.1 Emulsions in practice

Emulsions are dispersions of one liquid in another liquid with particle sizes typically in the range 1-10 μm. In order to obtain a stable emulsion a third component (emulsifier) has to be added to the emulsion. This emulsifying agent or emulsifier has mainly two functions: 1) to decrease the interfacial tension between the liquids, and thus enable the formation of the greatly extended interface compared with that of the two bulk phases, and 2) to stabilize the dispersed phase against coalescence. In most emulsions one of the liquid phases is water or an aqueous solution, and the other phase is an oil-like phase, which is almost completely immiscible with the water phase. Depending on which of these two phases is the continuous phase, the emulsion is called an oil-in-water (O/W) emulsion or a water-in-oil (W/O) emulsion.

The subject of emulsions is a broad field that includes many industrial applications and processes. In many of them only the stability of the emulsion is of importance. Some processes require the formation of stable emulsions, for instance in the production of mayonnaise. In other processes it is necessary to avoid the formation of an emulsion, for instance oil refinement.

The stability of emulsions is determined by four processes. The first one is creaming or sedimentation of the emulsion, caused by the density difference between the emulsion droplets and the continuous phase. The
second process is called coagulation or flocculation. In this process the single emulsion droplets are grouped together in larger clusters, in which the emulsion droplets keep their own identity. After this cluster formation, the droplets in a flock can flow together to one or more larger droplets. This process is called coalescence. The last named process which can occur is the so-called Ostwald ripening. This is a diffusion controlled process, that can occur if the oil phase is slightly soluble in the water phase. The oil of the smallest droplets will diffuse to the larger droplets through the continuous phase, resulting in a growing of the large droplets and a shrinking and finally disappearing of the small droplets.

In other applications in which emulsions occur, the flow properties are an important factor. Especially the oil industry is interested in flow of emulsions, particularly in flow of emulsions through porous media, since most of the world’s crude oil is produced in emulsion form [1]. Oil production occurs in three major stages. In the first stage the oil is produced by just pumping it out of the production well. After this stage, the oil has to be forced to the production well by injecting water in the oil field. This so-called water flooding results in a higher recovery, but still most of the crude oil (in some cases 65% to 70%) is left in the reservoir. The final tertiary stage in the oil recovery can be divided into two major groups, namely, recovery by thermal processes and by chemical flooding processes. In situ combustion, steam injection, wet combustion etc. fall into the first category, whereas caustic flooding, surfactant flooding, micellar-polymer flooding, CO2 flooding etc., belong to the second category of processes.

At the end of the water flooding, the residual oil is believed to be in the form of discontinuous oil ganglia or blobs trapped in the pores of the rocks of the reservoir. The two forces working on these oil ganglia are the viscous force and the capillary force. The ratio of these forces, expressed in the so-called capillary number \( N_c = \frac{v \eta}{\gamma} \) (where \( v \) is the velocity of the fluid, \( \eta \) the viscosity of the continuous phase and \( \gamma \) the interfacial tension between the oil droplet and the continuous phase) determines the microscopic displacement efficiency. At the end of the water flooding process \( N_c \) is as low as \( 10^{-6} \). In order to recover additional oil by a chemical flooding process, the capillary number has to be increased to around \( 10^{-3} \) to \( 10^{-2} \). Under
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High surface charge density
- Low interfacial tension
- Low interfacial viscosity
- High electrical repulsion between oil droplets and sand.

Low surface charge density
- High interfacial tension
- High interfacial viscosity
- Low electrical repulsion between oil droplets and sand.

Figure 1.1 The effect of the surface charge density of oil/brine interface on the oil displacement process [2].

practical reservoir conditions this change in capillary number can be achieved by drastically decreasing the interfacial tension at the oil/water interface.

The flooding techniques all have in common that, together with the oil, large amounts of waste water are produced. Separation of this water from the oil is necessary, because it hinders the refining process. For economical reasons and because of transporting problems, this separation must take place as near to the production site as possible. The separation of the oil and the water leaves about 1% oil dispersed in the water resulting in a stable O/W emulsion. Reusing this waste water for flooding or disposing it by injecting the emulsion in empty reservoirs is hardly possible, because of an enormous decrease of the permeability of the reservoir rocks on injection of the emulsion into it.

The processes of producing oil and the disposal of the waste water are problems related with the flow of emulsions through porous media. The most important factors influencing this flow are interfacial properties of the oil droplet and the porous material. Ultralow interfacial tension minimizes the work necessary to deform the droplet as it moves through the narrow necks of the pores. Interfacial viscosity has a large effect on the
coalescence of the drops in the pores. The three phase contact angle of the oil on the rock surface is a measure for the wettability of the rock. The oil displacement, which depends on this contact angle, will thus be influenced by the wettability of the rock surface.

Chaing et al. [2] showed that a large influence of the surface charge density of an oil ganglion can strikingly influence its displacement efficiency. High surface charge density leads to low interfacial tension, low interfacial viscosity and strong electrical repulsion between oil droplets and the porous material (Figure 1.1).

1.2 Topics described in this thesis

This thesis describes the transport of dilute stable O/W emulsions through packed beds of glass beads. Before the flow experiments could be carried out, measurements were performed to describe the stability of the emulsions used. The results of this investigation are described in chapter 2. Chapter 3 describes the experiments performed to study the transport of the emulsions through porous media. A microscopic model which describes the interaction of a single emulsion droplet with the porous material near a pore constriction is presented in chapter 4. As indicated in the previous section, the properties of the oil-water interface are very important. Chapter 5 describes some preliminary experiments for measuring the interfacial viscosity. Although it is at present too early to use these data in the primary subject of this thesis, they are included here, because it is thought that the present state of our knowledge forms a good starting point for future work.

1.3 References

Chapter 2

Stability of oil-in-water emulsions

2.1 Introduction

When the stability of emulsions is studied, the general interest goes to the emulsion breakdown processes. There are basically four ways in which a dispersion of liquid droplets in a continuous liquid can change.

The aim of the experiments described here, was the analysis of the influence of several factors such as electrolyte concentration and surfactant concentration on the stability of the emulsions used in the experiments with the porous media (Chapter 3).

2.1.1 Sedimentation

Sedimentation, the first phenomenon that relates to emulsion stability, is characterized by the formation of a droplet concentration gradient within the emulsion, while there is no change in the droplet size distribution. This can result in a, usually random, close-packed array of droplets at one end of the system. The concentration gradient is caused by external forces (gravitational, centrifugal, electrostatic) acting on the system. "Creaming" is the special case in which the droplets collect in a concentrated layer at the top of an emulsion.

The rate of sedimentation for nondeformable, noninteracting spheres of radius $r_p$ in a liquid of viscosity $\eta_0$ can be calculated by equating the gravitational force with the opposing hydrodynamic force, as given by
Stokes' law [1]. In applying Stokes' law, the assumption is introduced that the spherical particles do not interact during settling:

$$\frac{4}{3} \pi r^3 \Delta \rho g = 6 \pi \eta_0 r \rho v$$

(2.1)

where $\Delta \rho$ is the density difference between the particle and the bulk liquid, and $v$ the sedimentation rate. Thus,

$$v = \frac{2 \Delta \rho g r^2 \rho}{9 \eta_0}$$

(2.2)

If other external (e.g. centrifugal) forces are working on the system, the acceleration induced by this force must be substituted for $g$.

In almost all practical cases the sedimentation rate $v$ must be decreased to enhance the stability of the emulsion. Inspection of equation 2.2 indicates that this can be achieved by decreasing the density difference or by increasing the viscosity of the continuous phase.

The application of equation 2.2 however, depends on the validity of Stokes' law for the emulsion being considered. The assumption of a smooth surface is in most cases reasonable, but the question of deformability can cause complications. A liquid droplet moving within a second liquid phase may have an internal circulation imparted to it. Rybczynski [2] and Hadamard [3] treated this problem theoretically, resulting in an equation for the sedimentation rate in which the viscosity of the dispersed phase ($\eta$) appears:

$$v = \frac{2 \Delta \rho g r^2 \rho}{3 \eta_0 + \eta} + \frac{\eta_0}{3 \eta_0 + 2 \eta}$$

(2.3)

Frumkin and Levich [4] have considered the contribution of the interfacial viscosity, resulting in a modification of the Rybczynski-Hadamard equation (Eq. 2.3) by including a term for the Gibbs surface excess.

Another limitation which has to be considered for equation 2.2 (and 2.3) is that it strictly applies to noninteracting spheres. Equation 2.2 is thus only valid for very dilute emulsions. Most emulsions also show a wide variation in droplet size resulting in different sedimentation rates. These kinds of problems have been discussed by Greenwald [5].
2.1.2 Flocculation

It is characteristic of the flocculation process, that no change in the size of the primary droplets occurs, although large aggregates of droplets are formed in the emulsion. The individual droplets retain their identity within the aggregates. The process results from the existence of attractive forces between the droplets. In cases where these net attractive forces are relatively weak, reversible flocculation may be achieved. It can be shown that for a given system, a critical droplet number concentration exists, below which the emulsion is stable with respect to flocculation [6]. For strongly interacting droplets this critical droplet concentration is so low as to be practically insignificant. For systems which are thermodynamically unstable, flocculation can be effectively prevented if a large enough free energy barrier exists between the dispersed (deflocculated) state and the flocculated state. The emulsion is then stable in a kinetic sense.

The net interactive forces between the droplets consist of the London-Van Der Waals attractive forces, and by the electrical double-layer interactions. In addition, steric interaction may be caused by the emulsifying agents adsorbed in the interface between the two liquid phases. Since these last named effects are expected to be important especially in emulsion stabilized by non-ionic emulsifiers, we will restrict the discussion here to the London-Van Der Waals attraction and the electrical double-layer interactions.

2.1.2.1 London-Van Der Waals interactions

There exist two general approaches for the calculation of the interaction energy between condensed phases. The first, due to de Boer [7] and Hamaker [8] assume pairwise additivity of the forces between the molecules. The other more general approach, initiated by Lifshitz [9], considers the interactions in terms of macroscopic properties of the media.

Hamaker [8] calculated the interaction energy by integrating the attractive energy for two infinitesimal volume elements $dV_1$ and $dV_2$ separated by a distance $r$, over the total volumes $V_1$ and $V_2$ of the two particles:
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\[ V_A = -\frac{\lambda q^2}{r^6} \int \int dV_1 dV_2 \]  
\[ \text{(2.4)} \]

Here \( \lambda \) is the London-Van Der Waals constant, determined by the polarisability of the atoms and \( q \) is the number of atoms per unit volume. Hamaker assumed that the London parameter \( \lambda \) does not depend on the inter-atomic distance \( r \). For large values of \( r \) this assumption is not valid and the attractive interaction is then called retarded.

2.1.2.2 Electrical double-layer interactions

Emulsion droplets can possess an electrical surface charge due to adsorption of ions such as anionic surfactants. This charge is compensated by a distribution of the counter-ions in a diffuse layer around the particles: the electrical double-layer. When two droplets, carrying such a layer, approach each other, repulsion results from an overlapping of these diffuse layers. The electrical interactions of both flat plates and spheres were treated thoroughly by Verwey and Overbeek [10]. The electrostatic interaction free energy can be calculated analytically only in a few limited cases. One such an approximate equation was derived by Derjaguin and Landau [11]:

\[ G_E = 2\pi r \epsilon_r \epsilon_0 \psi_0^2 \ln(1 + e^{-\psi_0 h}) \]  
\[ \text{(2.5)} \]

where \( \epsilon_r \) is the relative dielectric constant of the medium, \( \epsilon_0 \) is the permittivity of free space, \( \psi_0 \) is the surface potential, \( h \) is the surface-surface separation, and \( \kappa \) is the reciprocal "thickness" (Debye length) of the electrical double layer. Equation 2.5 is only valid for low surface potentials and spheres large in comparison to \( \kappa^{-1} \).

For high surface potentials which occur in the systems described in this thesis, calculation of the energy of interaction is more complicated. For a description of this calculation see Verwey and Overbeek [10].

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2.1.3 Coalescence

A third process determining the stability of emulsions is coalescence. In this process droplets in a sediment or flock join together to form larger droplets. This results in a change of the droplet size distribution. The final state here is complete separation of the emulsion into two immiscible bulk liquids. Coalescence thus involves the elimination of the thin liquid film (of continuous phase), which separates two droplets in contact in an aggregate or a close-packed array. The forces to be considered here, therefore, are the forces acting within thin-liquid-film systems in general.

In figure 2.1 the film and the border region between two liquids are shown. Coalescence results from rupture of this film. This usually commences at a “spot” in the lamella, arising from thinning in that region. In order to understand the mechanism of the behaviour of these films two aspects need to be considered: 1) the nature of the forces acting across the film, and 2) kinetic aspects of local fluctuations in the film thickness.

Figure 2.1 Diagrammic representation of the thin film and border regions between two liquid droplets (α) in a continuous phase (β).
2.1.3.1 Forces across liquid films

The thin film region is considered to consists of two flat parallel interfaces, separated by a distance \( b \). At the end of the film there is a border or transition region where the interfaces have a high curvature, compared to the curvature of the droplet itself. A number of workers have attempted to measure the thickness of the liquid film. Sonntag et al. [12] have described a method for measuring O/W/O lamellae using light reflection.

As the forces acting across the film are considered, two regions of \( b \) are important. In the first region \( b > 2\delta \), where \( \delta \) is the thickness of the surfactant layers, forces of importance are the long-range Van Der Waals forces and the electrostatic repulsion.

2.1.3.2 Film rupture

The second region (\( b < 2\delta \)) is of main importance for coalescence. In this region steric interactions become important as the film tends to thin further, resulting in a very steeply increasing repulsive force. Film rupture requires breakdown of these steric interactions. A detailed investigation of film rupture is presented by Scheludko [13,14,15], Vrij [16], and Sonntag and Strenge [17].

Film rupture is a non-equilibrium effect and is associated with local thermal or mechanical fluctuations in the film thickness \( b \). Scheludko [15] introduced a theory in which arguments are presented for breakage of a film, if its thickness decreases below a critical thickness:

\[
b_{cr} = \left( \frac{A_{ham} \Pi}{3K^2 \gamma} \right)^{1/4}
\]

(2.6)

where \( A_{ham} \) is the net Hamaker constant, \( \gamma \) the interfacial tension, \( \Pi \) the disjoining pressure, introduced by Derjaguin [18], as a measure for the colloidal interactions in a thin film, and \( K \) a constant depending on \( R \), the radius of the (assumed) circular film zone.

Recently, new data on film rupture have been published by Exerowa et al. [19,20].
2.1.4 Ostwald ripening

If the two phases of an emulsion are mutually miscible to some extent, the average diameter of the emulsion can increase. If the initial emulsion system is truly monodisperse no effect of this slight solubility will arise. In polydisperse systems, larger droplets will form at the expense of smaller ones. This so called Ostwald ripening arises as a consequence of the Kelvin effect - the growth of the particles' solubility in media with a decrease in their size.

Kabalnov et al. [21] used a microscope to observe the Ostwald ripening process and concluded that this destabilizing effect must be taken into account when creating stable emulsions with a high polydispersity.

2.2 Measuring emulsion stability

Measuring emulsion stability is often a difficult problem, because the processes described in the previous sections, all take place simultaneously. Studying emulsion breakdown by flocculation or sedimentation is almost impossible without taking coalescence into account. In the next sections a number of experiments are presented in which the demulsification is studied by measuring flocculation kinetics.

One way of investigating flocculation of particles, is counting them. For rapid perikinetic (no shear) coagulation of a hydrophobic sol, Von Smoluchowski [23,24] derived an equation for the total number of particles (single or aggregated) as a function of time, in which absence of hydrodynamical interactions and absence of attraction or repulsion between the particles (unless they are in contact) is assumed:

\[ n = \frac{n_0}{1 + an_0 t} \]  
\[ (2.7) \]

where \( n_0 \) is the number of particles present in the system at \( t=0 \), and \( a \) is a rate determining constant for “rapid” coagulation for a monodisperse sol. The value of \( a \) can be calculated from the diffusion coefficient \( D \) of a particle with a radius \( r_p \):

\[ a = 8\pi Dr_p \]  
\[ (2.8) \]
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The demulsification process of an emulsion is not only determined by the formation of aggregates, but also by the number of particles that coalesce to form larger drops. Only the particles in an aggregate can coalesce. The average number of primary particles in an aggregate, either coalesced or not, can be calculated by application of Von Smoluchowski’s [23,24,25] theory. The number of primary particles not yet coagulated is given by:

\[ n_1 = \frac{n_0}{(1 + an_0t)^2} \]  \hspace{1cm} (2.9)

and the number of aggregates by (See appendix II):

\[ n_v = \frac{an_0^2t}{(1 + an_0t)^2} \]  \hspace{1cm} (2.10)

The total number of primary particles in all aggregates is (excluding the residual primary particles):

\[ n_0 - n_1 = n_0\left[1 - \frac{1}{(1 + an_0t)^2}\right] \]  \hspace{1cm} (2.11)

hence the average number of particles in a flock can be calculated:

\[ n_a = \frac{n_0 - n_1}{n_v} = 2 + an_0t \]  \hspace{1cm} (2.12)

The true average number of particles existing in an aggregate at time \( t \) is called \( m \). Due to the coalescence process, this number will always be less than \( n_a \). For very rapid coalescence \( m \) will be nearly 1.

To calculate the value of \( m \), an assumption about the coalescence kinetics has to be made. Observations by van den Tempel [26], performed on an emulsion with Aerosol OT (sodium di-2-ethylhexylsulphosuccinate) as emulsifier, showed that most aggregates in emulsions stabilized with Aerosol OT contain one large particle together with a few small ones, and are built up linearly. From this observation it is assumed that the coales-
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cence rate is proportional to \( m-1 \), the number of points of contact in an aggregate.

\[
\frac{dm}{dt} = an_0 - K(m-1)
\]

(2.13)

Here \( K \) is the first order coalescence rate constant. Integration of this equation with boundary condition \( m=2 \) at \( t=0 \) gives

\[
m - 1 = \frac{an_0}{K} + \left(1 - \frac{an_0}{K}\right)e^{-Kt}
\]

(2.14)

The total number of particles, either single or combined into aggregates, can be calculated by adding the number of "unreacted" primary particles to the number of particles in aggregates:

\[
n = \frac{n_0}{1+an_0} + \frac{an_0^2}{(1+an_0)^2} \left[ \frac{an_0}{K} + \left(1 - \frac{an_0}{K}\right)e^{-Kt} \right]
\]

(2.15)

For very dilute emulsions this equation can be simplified: the term \( \frac{an_0}{K} \) will be < 1, and after a longer time \( Kt \gg 1 \). With these two assumptions, the last term of equation 2.15 can be neglected and equation 2.7 can be applied.

In the formulation stated above it is assumed that no sedimentation occurs. In practice this can be achieved by matching the densities of the continuous phase and the emulsion droplets. Reddy et al. [27,28] investigated the coagulation behaviour of polydisperse emulsions which are subject to Brownian motion. They derived a general set of equations describing the effect of sedimentation and Brownian flocculation on the particle size distribution and concentration as a function of time and height. A cyclic change in particle size distribution was predicted by a population balance in a height section and observed experimentally.
2.3 Stability of emulsions stabilized with Aerosol OT or Sodium Oleate

In the following section a study of the stability of two kinds of emulsions is presented. Both types of emulsion have n-decane+tetrachloromethane mixtures as dispersed phase. The continuous phase of all emulsions used was an aqueous solution of sodium chloride or water. Variation of the volume ratio of decane+CCl₄ of the oil phase was used to match the densities of the dispersed phase and continuous phase.

In the case of the Aerosol OT (AOT) stabilized emulsions, the surfactant was dissolved in the water phase. For the emulsions stabilized with sodium oleate (NaOl) a special preparation procedure was used which will be described in the experimental section.

2.3.1 Experimental

Prior to the preparation of an emulsion the dispersed phase was made by mixing n-decane (Janssen Chemica, 99+%, purified on an alumina column, or Merck, zur Synthese, purified by distillation followed by purification on an alumina column) and tetrachloromethane (Merck, pro analysi) such as to give to the mixture a specified density. In the case of sodium oleate, an amount of oleic acid (Merck, reinst) was dissolved in the decane+CCl₄ mixture.

For the AOT stabilized emulsions a solution of Aerosol OT (Sigma Chemical Company, 10% w/v solution, used as received) in water with a concentration such that after preparation of the emulsion the desired concentration was reached. When preparing a NaOl emulsion, a solution was made of sodium hydroxide (Merck Titrisol) in such a concentration that after the emulsion preparation all the oleic acid dissolved in the oil phase would be neutralized and the pH of the emulsion would be about 10.

To prepare an emulsion, 5 ml of the oil mixture was dispersed in 495 ml water phase (AOT solution or NaOH solution) using an Ystral X40 dispersing unit with a generator for media with low viscosities (diameter 20 mm). The resulting emulsions had a logarithmic normal distribution between 1 µm and 8 µm. The average particle size was 2.5 µm.
The demulsification process was started by adding 5 ml of a concentrated solution of sodium chloride (Merck, *pro analysi*) to 25 ml of the previously prepared emulsion, and was performed as near as possible perikinetically (no shear). The change in particle concentration and particle size as a function of time was measured using a Coulter Counter (Model ZM, equipped with a Channelyzer 256 and a Coulter Range Expander). At specific times a 400 µl sample of the emulsion was taken and diluted in 25 ml Isoton II™ (electrolyte solution for Coulter Counter measurements). Because the densities of the dispersed phase and the continuous phase do not exactly match, it was necessary to homogenize the emulsion before sampling by shaking it very cautiously for a few seconds. The concentration of the particles in the diluted sample was determined by counting the number of droplets in 500 µl diluted emulsion. This particle concentration was then used to calculate the particle concentration of the original emulsion.

The Coulter Counter technique has the advantage that a single large particle and a flocculated particle with the same volume give the same response at the instrument. This results in a measurement of the coagulation kinetics which is not affected by the coalescence rate.

Interfacial tensions of the emulsions were measured using a Krüss Spinning Drop Tensiometer. The dimensions of the oil droplet in the rotating capillary of the tensiometer were measured by photography.

Zeta-potentials of NaOl stabilized emulsions used, were measured with a Malvern Zetasizer III.

The densities of the decane+CCl₄ mixtures were determined with a Mettler/Paar DMA55 digital densitometer at 25°C.

2.3.2 Results and discussion

2.3.2.1 AOT-stabilized emulsions

Figure 2.2 shows the densities of the decane+CCl₄ mixtures as a function of the molar fraction CCl₄. The results show good correspondence with data measured by Jain *et al.* [29]. From this figure the composition of the dispersed phase is calculated for a given density.
Figure 2.2 Density of n-decane/CCl₄ mixtures as function of their composition. ▲ This study, ● Jain et al. [27]

Table 2.1 Effective collision frequency for AOT stabilized emulsions.

<table>
<thead>
<tr>
<th>[NaCl] (mol/l)</th>
<th>a (ml/cts s)</th>
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</thead>
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<tr>
<td>0.1057</td>
<td>0.2×10⁻¹²</td>
</tr>
<tr>
<td>0.2114</td>
<td>7.0×10⁻¹²</td>
</tr>
<tr>
<td>0.2476</td>
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</tr>
</tbody>
</table>

Figure 2.3 shows some typical coagulation curves for an AOT stabilized emulsion. In this experiment the AOT concentration was kept constant and the NaCl concentration was varied. For the high NaCl concentrations the demulsification process was fast and did not depend on the electrolyte concentration, as expected for concentrations above the critical coagulation concentration (CCC). For the low NaCl concentration (0.1057 M) the emulsion seemed to be relatively stable. The number of particles decreased about 60% after 7 hours, which is rather slow compared to a decrease of 80% after 1 hour for the high NaCl concentrations. Table 2.1 shows the coagulation rate constants a calculated from the results shown in figure 2.3. The values have the same magnitude as those found by Van Den Tempel [26]. Numerical simulation of a coagulation process using Von
Smoluchowski's theory, results in a theoretical value for the coagulation rate constant of $5.6 \times 10^{-14}$ ml/cts s. This value is much lower than the values observed. As will be seen later, this is probably caused by a faster coagulation resulting from the shaking of the emulsion before taking the sample.

Figure 2.4 shows similar results for a somewhat higher volume fraction dispersed phase (2.5%). As can be seen, at high electrolyte concentrations, the initial particle concentration $n_0$ is lower compared to the lower electrolyte concentrations. It can be concluded that in the initial stages of the demulsification process the coagulation proceeds very fast, since all the emulsions are prepared from a single standard emulsion. In figure 2.5, the average particle diameter after 5 minutes, calculated from the volume fraction dispersed phase and the particle concentration, is shown. The diameter of the emulsion droplets at the high NaCl concentration indicate the formation of doublets and triplets. This rapid coagulation at the beginning of the demulsification process leads to an apparently lower initial particle concentration at the higher electrolyte concentrations.
Figure 2.4 Reciprocal particle concentration of emulsions stabilized with AOT versus time. Volume fraction dispersed phase: 2.5%.  + [NaCl] = 0.04 M; ■ [NaCl] = 0.09 M; ◆ [NaCl] = 0.13 M; ▼ [NaCl] = 0.22 M; ● [NaCl] = 0.26 M; ▲ [NaCl] = 0.44 M.

Figure 2.5 Number average particle diameter of AOT stabilized emulsions, calculated from the volume fraction dispersed phase (2.5%) and the initial number of particles no.
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Figure 2.6 Effective collision frequencies calculated from the curves in figure 2.4.

The collision frequencies calculated from the experiments of figure 2.4 are plotted on a logarithmic scale versus the NaCl concentration in figure 2.6. At sodium chloride concentrations above 0.5 M, the collision frequency tends to level off to a constant value: the coagulation process becomes independent of the sodium chloride concentration. This is a rather high value compared to the usual value of 0.15 M for solid particles. Below this concentration the coagulation rate rapidly decreases, with decreasing electrolyte concentration. All these results indicate that the emulsions are stabilized electrostatically. Figure 2.7 shows the $\zeta$-potentials for the AOT stabilized emulsion.

Figures 2.8 to 2.11 show the results of coagulation experiments performed to measure the influence of the composition of the dispersed phase. The three curves in each figure are again the reciprocal particle concentration versus time for different NaCl concentrations. The collision frequencies calculated from these experiments are shown in figure 2.12 as a function of the mole fraction tetrachloromethane. The values of the rate constants increase as the density difference between the oil phase and the continuous phase decreases.
This is a strange effect which corresponds to the results of microgravity coagulation experiments of Krutzer [31], where a faster coagulation under microgravity than under 1-g conditions is observed. An explanation for this effect may be found in the slower sedimentation of the particles: The particles will be longer in contact during a collision, and the probability of cluster formation will be higher. This gives a higher coagulation rate if the density difference between the particles and the continuous phase is smaller.

The influence of the interfacial tension on the demulsification rate is small. The coagulation rate constant increases for increasing \( x_{\text{CCl}_4} \), although the interfacial tension does not change very much. Figure 2.13 shows the interfacial tension versus the molar fraction CCl\(_4\) of the dispersed phase. At a NaCl concentration of 0.1 molar the interfacial tension does not show large variations when varying \( x_{\text{CCl}_4} \). For the concentration of 0.2 M the interfacial tension increases with increasing molar fraction CCl\(_4\).

At lower salt concentrations the interfacial tension of the system decreases drastically if the dispersed phase contains more CCl\(_4\). Figure
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Figure 2.8 Reciprocal particle concentration. $x_{CCl_4} = 0.4$. ▲ [NaCl] = 0.3 mol/l; ● [NaCl] = 0.2 mol/l; ▽ [NaCl] = 0.15 mol/l

Figure 2.9 Reciprocal particle concentration. $x_{CCl_4} = 0.3$. Symbols see figure 2.8.

Figure 2.10 Reciprocal particle concentration. $x_{CCl_4} = 0.25$. Symbols see figure 2.8.

Figure 2.11 Reciprocal particle concentration. $x_{CCl_4} = 0.2$. Symbols see figure 2.8.
Figure 2.12 Effective collision frequency of AOT stabilized emulsions as a function of NaCl concentration and CCl4 content of the dispersed phase, calculated from the data in figures 2.7 to 2.10. ▲ [NaCl] = 0.3 mol/l; ● [NaCl] = 0.2 mol/l; ▼ [NaCl] = 0.15 mol/l.

Figure 2.13 Interfacial tension for high NaCl concentrations as a function of the dispersed phase composition. ▲ [NaCl] = 0.1 M; ● [NaCl] = 0.2 M. [AOT] = 0.00018 M.
2.14 shows the interfacial tension for a series of sodium chloride concentrations. The interfacial tension of this system drops for all three concentrations to a very low value. At these low values formation of microemulsions could be expected, but because of the low oil phase concentration we could not see whether they were formed.

The influence of the NaCl concentration on the interfacial tension is shown in figure 2.15: a very sharp minimum is observed at a NaCl concentration of 0.05 mol/l. This result shows good correspondence with the results reported by Aveyard et al. [32,33]. They have studied the effects of salt, temperature and alkane on the interfacial tension and derived an equation for the variation of the interfacial tension with the salt concentration or the temperature.

2.3.2.2 Sodium Oleate stabilized emulsions.

Emulsions stabilized with sodium oleate show similar behaviour towards coagulation kinetics. Figures 2.16, 2.17 and 2.18 show the results
Figure 2.15 Interfacial tension of the n-decane+CCl4/water interface as a function of the NaCl concentration of the aqueous phase. [AOT] = 0.00043 M.

of the experiments performed. Again the reciprocal particle concentration is proportional with time. Figure 2.19 shows that the NaOl stabilized emulsions are more stable than the AOT stabilized emulsions. The critical coagulation concentration here is around 0.3 mol/l NaCl. The coagulation rate constants have the same magnitude as for emulsions stabilized with AOT. Figure 2.20 shows the measured ζ-potentials for various surfactant concentration as a function of the sodium choride concentration. These results are in good agreement with the CCC value of 0.3 mol/l.

Experiments where both types of emulsions were used for flow through porous media (see next chapter) indicated also a higher interfacial elasticity of the NaOl-stabilized emulsions: these emulsion did not coalesce in the porous medium in contrast to the AOT-stabilized emulsions.

In figure 2.21 the particle size distribution of the emulsions is shown. The mean particle size decreases and the distribution is narrower for higher sodium oleate concentrations. The mean particle diameter seems to become constant above NaOl concentrations of 5 mmol/l.
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Figure 2.16 Reciprocal particle concentration. $[\text{NaOl}] = 0.5 \text{ mmol/l}$; $[\text{NaCl}] = 0.20 \text{ mol/l}$; $[\text{NaCl}] = 0.27 \text{ mol/l}$; $[\text{NaCl}] = 0.22 \text{ mol/l}$; $[\text{NaCl}] = 0.23 \text{ mol/l}$; $[\text{NaCl}] = 0.30 \text{ mol/l}$; $[\text{NaCl}] = 0.40 \text{ mol/l}$; $[\text{NaCl}] = 0.27 \text{ mol/l}$; $[\text{NaCl}] = 0.25 \text{ mol/l}$; $[\text{NaCl}] = 0.50 \text{ mol/l}$; $[\text{NaCl}] = 0.40 \text{ mol/l}$.

Figure 2.17 Reciprocal particle concentration. $[\text{NaOl}] = 1.0 \text{ mmol/l}$; $[\text{NaOl}] = 2 \text{ mmol/l}$; $[\text{NaCl}] = 0.25 \text{ mol/l}$; $[\text{NaCl}] = 0.27 \text{ mol/l}$; $[\text{NaCl}] = 0.30 \text{ mol/l}$; $[\text{NaCl}] = 0.40 \text{ mol/l}$.

Figure 2.18 Reciprocal particle concentration. $[\text{NaOl}] = 2 \text{ mmol/l}$; $[\text{NaOl}] = 2 \text{ mmol/l}$; $[\text{NaOl}] = 2 \text{ mmol/l}$; $[\text{NaOl}] = 2 \text{ mmol/l}$; $[\text{NaOl}] = 2 \text{ mmol/l}$; $[\text{NaOl}] = 2 \text{ mmol/l}$.
Figure 2.19 Effective collision frequency calculated from figures 2.15, 2.16 and 2.17. ▲ [NaOl] = 0.5 mmol/l; ● [NaOl] = 1.0 mmol/l; ▼ [NaOl] = 2.0 mmol/l.

Figure 2.20 ζ-potentials of emulsions stabilized with sodium oleate. ▲ [NaOl] = 0.5 mmol/l; ● [NaOl] = 1.0 mmol/l; ▼ [NaOl] = 2.0 mmol/l.
Figure 2.21 Mean particle diameter of the emulsions as a function of the sodium oleate concentration. Bars indicate one standard deviation.

Figure 2.22 Interfacial tension water/n-decane as a function of the sodium oleate.
Figure 2.23 Summary of the coagulation rate coefficients as a function of the sodium chloride concentration. ♦ [AOT]=0.42 mmol/l; ▲ [NaOl]=0.5 mmol/l; ● [NaOl]=1.0 mmol/l; ▼ [AOT]=2.0 mmol/l.

Figure 2.22 shows the interfacial tension of the water/n-decane interface. All the concentrations measured are below the cmc, which is about 1 mmol/l. At low concentrations a large deviation from the real values is observed. The actual values were too high to measure using the spinning drop technique.

2.3.3 Comparison of the behaviour of the emulsions

Figure 2.23 summarizes the results of the coagulation rate coefficients $\alpha$ of both types of emulsion. The $\zeta$-potential data give the expectation that both emulsions should be about equally stable. If there would be differences, the slightly larger $|\zeta|$ value for AOT stabilized emulsions should lead to the expectation of a slower coagulation for AOT than for NaOl stabilized emulsions (if the Hamaker constant may be taken to be equal). The sodium oleate emulsion however shows a much more pronounced change in the rate coefficient with change in the NaCl concentration, than the AOT emulsion. The difference in stability is confirmed in the next chapter, where
Figure 2.24 Definition of symbols used to calculate the interaction between spherical particles and between deformed spherical particles.

experiments with these emulsions flowing through porous media are discussed.

The values of the coagulation rate coefficient $\alpha$ found, are surprisingly much larger as the values expected on the basis of equation 2.8, if for the diffusion coefficient the Einstein value $D = kT/6\pi\eta r_p$ is taken. This would lead to an $\alpha$ value of $5.8 \times 10^{-12}$ ml/(cts s).

The following effects might explain this phenomenon:

1. Creaming or sedimentation of the emulsion droplets brings about a larger droplet concentration for at least part of the droplets, whereas the $\alpha$ values mentioned in figure 2.23 refer to emulsions with a homogeneous droplet distribution. This argument however, is refuted by the results presented in figure 2.12: the $\alpha$ values are especially large for emulsions near matching of the densities of the disperse and continuous phases.

2. The deformation of the particles may lead to a decreased influence of electrostatic repulsion because a type of coagulation as depicted in figure 2.24 becomes possible. Results of calculated interaction energies for deformed and non-deformed particles are described below.

3. The fact that we are dealing not with rigid spherical particles, but with deformable droplets may lead to a larger diffusion coefficient at
infinite dilution, than expected from the Einstein equation. The importance of this effect is difficult to estimate; however a factor near 100 a shown in figure 2.23 is not very probable.

4. Attraction between the dispersed droplets at large electrolyte concentration leads to an increased coagulation compared with the Von Smoluchowski prediction (eq. 2.8). This effect can be estimated from the theory of Fuchs [35], combined with the Hamaker theory on attraction between spherical particles [8], and the Clayfield et al. [34] treatment of the retardation of the attractive forces. The correction factor $\alpha$ on the approach given for the non-interaction case (original Von Smoluchoski theory) is given by (see Spielman [30]):

$$\frac{1}{\alpha} = \left(1 + \frac{a_2}{a_1}\right) \int \frac{D_{12}^{-\infty} e^{-V/ds} d\delta}{1 + \delta^2}$$

(2.16)

In the evaluation of this integral, a Hamaker constant of $4.6 \times 10^{-20}$ J was chosen. For this value of the Hamaker constant, the interaction energy for NaO1 stabilized emulsions does not become repulsive for sodium chloride concentrations above 0.2 mol/l, when undeformed droplets characterized by the $\zeta$-potentials found are considered. However, calculations were also performed at other Hamaker constant values. The Hamaker constant was taken the same for convenience for both types of emulsion. This may not exactly be true; it is likely that the values are somewhat different, since the composition of the droplets was not exactly the same. However, this difference was neglected.

The correction factor expressed by equation 2.16 has values in the range from near 2.0 (for rigid particles equally sized) to about 6.5 (for rigid particles with a radius ratio of 2.15). For deformable particles $D_{12}^{-\alpha}D_{12}$ may be lower than the values calculated for rigid particles, because the internal movement of the liquid in the droplet will decrease the hydrodynamic interaction. In the absence of hydrodynamic interaction, the integral takes values ranging from unity to about 3.4 for equal sized and unequal sized ($r_2/r_1=2.15$) respectively. The results of these calculations are summarized in appendix I at the end of this chapter.
5. Matching of densities was not perfect, thus sampling required homogenization of the emulsion be cautious shaking. This naturally was required especially if there was a distinct density difference between the phases. Estimation of the average shear rate (appendix III) showed that the effect of the shaking was much larger than expected initially, and actually it determines the coagulation process completely.

To investigate whether the lower interfacial tension values found for the AOT stabilized emulsions might explain the stability difference, interaction energies between two spherical droplets and two deformed droplets (figure 2.24) were calculated. Thus the energetic feasibility of a coagulation process leading to a droplet pair with flat contact area is investigated. By doing so, the very large repulsion calculated for two spheres in near contact could be avoided, unless of course the interfacial energy needed for the large liquid-liquid interface in the case of flat contact area would be prohibitive.

The total interaction energy between two spherical particles is determined by the attractive London-Van Der Waals forces and the repulsive electrostatic forces. The attractive forces were calculated using the approach of Clayfield et al. [34] for retarded London-Van Der Waals interaction between two spherical particles. The repulsive forces were calculated using the tabulated results of Verwey and Overbeek [10]. Using this approach the Debye-Hückel approximation is avoided. The calculations thus compare the interaction energy of undeformed droplets (interaction potential given by the DLVO theory) with the interaction energy of droplets deformed such as to have flat contact area, where both droplets are separated such as to be in the secondary minimum for flat plates.

The results of these calculations are summarized in figure 2.25 for the AOT stabilized emulsion and in figure 2.26 for the NaO1 stabilized emulsion.

To calculate the interaction energy for deformed droplets, flat surface interaction was used between the deformed sections of the spheres. The distance between the two deformed surfaces $h_{II}$ was taken as the distance at the secondary minimum for flat surface interaction. The distance between the particle centres $r$ can be calculated from the distance between the surfaces, the deformed radii and the angles $\theta_1$ and $\theta_2$ describing the flattened section of the drops:
Figure 2.25 Interaction energies for AOT stabilized emulsions calculated for undeformed droplets. Particle size 2.34 μm; $A_{ham} = 4.6 \times 10^{-20}$ J. 

- $[\text{NaCl}] = 0.05$ mol/l; ○ $[\text{NaCl}] = 0.10$ mol/l; ▼ $[\text{NaCl}] = 0.2$ mol/l; 
- $[\text{NaCl}] = 0.4$ mol/l; ■ $[\text{NaCl}] = 0.5$ mol/l.

Figure 2.26 Interaction energies for NaOl stabilized emulsions calculated for undeformed droplets. Particle size 2.34 μm; $A_{ham} = 4.6 \times 10^{-20}$ J. 

- $[\text{NaCl}] = 0.05$ mol/l; ● $[\text{NaCl}] = 0.10$ mol/l; ▼ $[\text{NaCl}] = 0.2$ mol/l; 
- $[\text{NaCl}] = 0.4$ mol/l; ■ $[\text{NaCl}] = 0.5$ mol/l.
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\[ r = h_{II} + b_1 \cos \theta_1 + b_2 \cos \theta_2 \]  
(2.16)

The circular flattened section of the droplets must have the same radius for both particles:

\[ b_1 \cos \theta_1 = b_2 \cos \theta_2 \]  
(2.17)

The volumes of the deformed particles must be the same as the volume of the undeformed particles. So,

\[ \frac{4}{3} \pi a_1^3 = \frac{1}{3} \pi b_1^3 (2 + 3 \cos \theta_1 - \cos^3 \theta_1) \]  
(2.18)

\[ \frac{4}{3} \pi a_2^3 = \frac{1}{3} \pi b_2^3 (2 + 3 \cos \theta_2 - \cos^3 \theta_2) \]  
(2.19)

If \( a_1, a_2, h_{II} \) and \( r \) are given, equations 2.16 to 2.19 can be used to solve the parameters \( b_1, b_2, \theta_1 \) and \( \theta_2 \).

The total interaction due to deformation of the droplets can then be calculated by adding the interaction of the two flattened areas of the droplets and the energy gain caused by the deformation of the surface:

\[ V_{int}^H = \gamma \Delta A + \pi (b_1 \sin \theta_1)^2 V_{sec.min}^{fs} \]  
(2.20)

Here \( \gamma \) is the interfacial tension, \( \Delta A \) the area change due to deformation and \( V_{sec.min}^{fs} \) the flat surface interaction energy per unit surface area at the secondary minimum.

The area change due to the deformation will be

\[ \Delta A = 2\pi b_1^2 (1 + \cos \theta_1) + 2\pi b_2^2 (1 + \cos \theta_2) + 2\pi (b_1 \sin \theta_1)^2 - 4\pi a_1^2 - 4\pi a_2^2 \]  
(2.21)

Using this equation together with 2.20 gives the final relation to calculate the interaction between the deformed emulsion droplets.

Figures 2.27 and 2.28 respectively show the results for AOT and NaOL stabilized emulsions. For both types of emulsion the surface energy gain by deformation is much smaller than the colloidal interactions. The resulting data for the deformed droplets are all negative. Hence if all particles
Figure 2.27 Interaction energies for AOT stabilized emulsions calculated for deformed droplets. Particle size 2.34 μm; $A_{ham} = 4.6 \times 10^{-20}$ J.

Figure 2.28 Interaction energies for NaOl stabilized emulsions calculated for deformed droplets. Particle size 2.34 μm; $A_{ham} = 4.6 \times 10^{-20}$ J.
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would deform, no stable emulsions would be formed for the systems discussed here. From figure 2.22 it can be concluded that the AOT emulsion is less stable than the NaOl emulsion.

We can explain the data on the assumption that at low sodium chloride concentrations the droplets of the AOT emulsion are easier deformable, resulting in a less steep increase of the coagulation rate constant with increasing NaCl concentration. This effect must be a kinetic effect: not all pairs of drops will deform, otherwise no electrostatic stabilizing effect would be found.

For the high sodium chloride concentrations both emulsions have about the same stability. The interaction energy of the NaOl stabilized emulsion will be totally attractive if the NaCl concentration is above 0.4 mol/l at the value of the Hamaker constant chosen.

In order to check these considerations, interfacial rheology data should be measured. These data describe the deformability of the emulsion droplets. In chapter 5 a first step to measure such data is described. Unfortunately, due to instrumental difficulties, we were not able to perform real measurements to confirm the above hypothesis.

2.4 References

[1] G.G. Stokes, Phil. Mag., 1 (1851) 337
[31] L.L.M. Krutzer, H.N. Stein, to be published.
[37] L.L.M. Krutzer, H.N. Stein, to be published.
Appendix I. Correction of the Von Smoluchowski perikinetic coagulation frequency for colloid chemical and hydrodynamical interactions.

The Von Smoluchowski collision frequency, derived for absence of colloid chemical and hydrodynamical interactions, is given by equation 2.8:

\[ a = 4\pi D_{12}^{\infty}(a_1 + a_2) \]  

(I.1)

Here \( D_{12}^{\infty} \) is the mutual diffusion coefficient of two particles with radii \( a_1 \) and \( a_2 \) respectively. The derivation \([22]\) starts from considering the flux by diffusion \( n_2 \) of particles of type 2 towards one particular particle of type 1, through a spherical surface (radius \( r \)) around the particle of type 1:

\[ J_{12} = 4\pi r^2 D_{12}^{\infty} \frac{dn_2}{dr} \]  

(I.2)

where \( n_2 \) is the number of particles of type 2 per unit volume.

When colloid chemical and hydrodynamical effects are no longer neglected, \( D_{12} \) becomes dependant of \( r \), and in addition to the diffusion flux there is also a flux caused by the potential energy gradient \( \frac{dV}{dr} \):

\[ J_{12} = 4\pi r^2 D_{12} \frac{dn_2}{dr} + 4\pi r^2 \frac{n_2}{f} \frac{dV}{dr} \]  

(I.3)

where \( f \) is the friction factor = \( D_{12}/kT \). Eliminating \( f \), we obtain:

\[ J_{12} = 4\pi r^2 D_{12} \frac{dn_2}{dr} + 4\pi r^2 \frac{n_2 D_{12}}{kT} \frac{dV}{dr} \]  

(I.4)

A general solution \([22]\) leads to:

\[ J_{12} = \frac{4\pi n_2}{\int_0^\infty \frac{1}{D_{12}} \frac{\exp\left(-\frac{V}{kT}\right)}{r^2} dr} a_1 + a_2 \]  

(I.5)
Introducing \( s = \gamma a_1 \) as dimensionless variable, we obtain:

\[
J_{12} = \frac{4\pi n_2^\infty}{\infty} \int_{a_1}^{a_2} \frac{1}{D_{12}} \frac{1}{s^2} e^{\frac{\nu kr}{s}} \, ds
\]

This leads to:

\[
a = \frac{J_{12}}{n_2^\infty} = \frac{4\pi}{\infty} \int_{a_1}^{a_2} \frac{1}{D_{12}} \frac{1}{s^2} e^{\frac{\nu kr}{s}} \, ds
\]

For comparison with equation A.1, we write

\[
a = \frac{4\pi D_{12}^\infty (a_1 + a_2)}{a_1 + a_2} \int_{a_1}^{a_2} \frac{D_{12}^\infty}{D_{12}} e^{\frac{\nu kr}{s^2}} \, ds
\]

in which the denominator can be calculated by numerical integration, using the Spielman theory [30] for \( \frac{D_{12}^\infty}{D_{12}} \); the Clayfield c.s. [34] theory for (retarded) London-Van Der Waals attraction, and the Verwey and Overbeek [10] electrostatic repulsive energy values for flat plates incorporating them in a numerical integration of the repulsion for spherical particles. By so doing, the restriction to low surface potential values as in the Derjaguin formula [22] is avoided.

The calculations refer to collisions between a basic droplet (radius 2.34 \( \mu \)m), with droplets formed by coalescence of \( n \) basic droplets. The results are given in table A.1. In the table two values are tabulated: I without
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Table A.1 Correction factor for the Von Smoluchowski collision frequency.

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hydrodynamical interaction (i.e. $\frac{D_{12}^\infty}{D_{12}} = 1$); II with hydrodynamical interaction being taken into account.
Appendix II. Derivation of equation 2.10

Relation 2.10 can be derived as follows: The number of particles per unit volume composed of \( k \) primary particles is given by

\[
n_k = \frac{n_0(an_0t)^{k-1}}{(1 + an_0t)^{k+1}}
\]

We are interested in the total number of aggregates per unit volume:

\[
n_{aggregates} = \sum_{k=2}^{\infty} n_k = n_0 \sum_{k=2}^{\infty} \frac{(an_0t)^{k-1}}{(1 + an_0t)^{k+1}}
\]

\[
n_0 \left[ \frac{an_0t}{(1 + an_0t)^3} + \frac{(an_0t)^2}{(1 + an_0t)^4} + \frac{(an_0t)^5}{(1 + an_0t)^5} + \ldots \right] =
\]

\[
\frac{an_0t}{(1 + an_0t)^3} \left[ 1 + \frac{an_0t}{1 + an_0t} + \frac{(an_0t)^2}{(1 + an_0t)^2} + \ldots \right] =
\]

\[
\frac{an_0^2 t}{(1 + an_0t)^3} = \frac{1}{1 - \frac{an_0t}{1 + an_0t}}
\]

\[
\frac{an_0^2 t}{(1 + an_0t)^2}
\]

(II.2)
Appendix III. Estimation of the average shear rate due to shaking of the emulsion.

To give an estimation for the shear rate a second term has to be added to the particle flux in the Von Smoluchowski equation:

\[ J_{12} = 4\pi r^2 D \frac{dn}{dr} + \frac{4}{3} \gamma n(a_1 + a_2)^3 \]  

(III.1)

Here the second term gives the contribution of the shear rate to the flux of particles. To estimate the influence we assume that the diffusive flux of the particles can be neglected:

\[ \frac{dn}{dt} = -\frac{1}{2} J_{12} n = -\frac{2}{3} \gamma n^2(a_1 + a_2)^3 \]  

(III.2)

Integration of this equation gives an approximate expression for orthokinetic coagulation:

\[ n = \frac{n_0}{(1 + a n_0 \gamma)} \]  

(III.3)

Here \( n_0 \) is the initial particle concentration and \( a \) is the coagulation rate coefficient defined by:

\[ a = \frac{2}{3} \gamma (a_1 + a_2)^3 \]  

(III.4)

Assuming that the particle radius is 2.5 \( \mu \)m and \( a \) in the magnitude of the measured values (\( a = 10^{-17} \text{ m}^3 \text{ s}^{-1} \)), equation III.4 gives a value for the shear rate of 0.12 s\(^{-1}\). If the time average shear rate has this magnitude the particle flux due to the shear would be much larger than the diffusive flux.

Estimation of the average shear rate due to homogenization before measurements, averaged over time and emulsion volume is done as follows. Homogenization was achieved by cautious stirring. It is assumed that this results in a rigid rotation of the inner core of the emulsion, while there is
Figure III.1 Stirred emulsion seen from the top. Region I: rigid rotation region. $\omega = \omega_i$, $\dot{\gamma} = 0$. Region II: shear region, $\omega$ decreases with increasing $r$ value; at $r = R_o$ the liquid is in rest.

an outer region in which there is a shear. [36,37]. In figure III.1 this is illustrated.

The ratio $f = \frac{R_i}{R_o}$ will depend on time and rotation rate. For convenience it is assumed to be constant here. If laminar flow occurs in region II, the shear rate is given by:

$$\dot{\gamma} = r \frac{d\omega}{dr} = \frac{M}{2\pi \eta r^2} \quad (\text{III}.5)$$

Here $h$ is the height of the liquid, $\eta$ the viscosity of the liquid and $M$ the moment exerted by the vessel on the emulsion. The moment $M$ is determined by the value of $\omega_i$, the angular velocity of region I:

$$M = \frac{4\pi h \eta \omega_i R_o^2}{\frac{1}{f^2} - 1} \quad (\text{III}.6)$$

Therefore
The average value of the shear rate over region II at any time is given by:

\[ \langle \dot{\gamma} \rangle_{V} = \frac{R_{i}}{R_{p}} \int_{R_{p}}^{R_{i}} \frac{\dot{\gamma} 2\pi r dr}{2\pi rdr} \]

The average over the whole volume including region I is then given by

\[ \langle \dot{\gamma} \rangle = -\frac{4\omega_L}{f^2 - 1} \ln f \]

For calculating the time average value we assume \( \omega_i = \omega_{i,0}e^{-kt} \) with \( k = 0.23 \) (estimated half value time of \( \omega_i \) about 3 s). We then obtain:

\[ \langle \dot{\gamma} \rangle_{V,t} = \frac{1}{\Delta t} \int_{0}^{\Delta t} \langle \dot{\gamma} \rangle_{V} dt \]

where \( \Delta t \) is the time between two successive samplings of the emulsion (\( \geq 300 \) s). We finally obtain:

\[ \langle \dot{\gamma} \rangle_{V,t} = \frac{4\omega_{i,0}}{f^2 - 1} \ln f * \frac{1}{k\Delta t} \left( e^{-k\Delta t} - 1 \right) \]

With \( f = 0.8 \), \( \Delta t = 300s \), \( \omega_{i,0} = 6s^{-1} \) and \( k\Delta t >> 1 \) we obtain an average shear rate of 0.07 s\(^{-1}\). This value is only slightly dependent on the value of \( f \) assumed. The most debatable assumption in this derivation is that of laminar flow. In reality, there will be Taylor vortex flow in region II which will increase the effective average shear rate value.
From the derivation above can be concluded that the coagulation rate was mainly determined by the shaking of the emulsion. The main difference between the Aerosol OT stabilized emulsion and the sodium oleate stabilized emulsion still can be ascribed to the deformation effects explained in section 2.3.3.
Chapter 3

Transport of emulsions through porous media

3.1 Introduction

In the past much research has been done on multiphase flow through porous media. Most of the liquid-liquid studied systems are unstable coalescing emulsions or, to a minor degree, bicontinuous phases. Spielman and Goren [1] reviewed the progress on the studies of the coalescence of liquid-liquid suspensions by porous media and presented theoretical description of this process.

Flow of stable emulsions through porous media is much less studied. McAuliffe [2] studied the ability of emulsions to decrease the heterogeneity of oil reservoirs and thus improving the oil recovery. He found that large permeability reductions were possible by injecting emulsions with droplet sizes somewhat larger than the pore sizes. He also found that the permeability reduction was largest in high permeability cores and that the permeability decrease was almost irreversible.

Devereux [3] presented a theoretical description for the flow of an emulsion through a porous core, in which the permeability reduction is fully ascribed to the retention of oil droplets caused by retarding forces due to capillary effects. His model gives a good description of the experimental data [4], but the irreversibility of the permeability reduction cannot be explained.
Alvarado and Marsden [5] described the flow of emulsions through porous media as the flow of power-law liquids through a bundle of capillaries. This model also cannot explain the irreversibility of the permeability reduction.

Soo and Radke [6,7] developed a model, based on a model for deep bed filtration, in which the permeability reduction is caused by two filtration effects. The most important effect is straining: Oil droplets clog in pore constrictions of sizes smaller than their own by lodging between the grains of the porous medium. This has a large effect on the permeability, since all connected pores are blocked too for emulsion flow. The second effect is the interception of oil droplets by trapping in circulation eddies or attachment to pore walls due to van der Waals forces. In the model three phenomenological parameters are important: The filter coefficient, the capture efficiency and the flow redistribution parameter.

In this chapter experiments are described with flow of stable emulsions through porous media. From these experiments it can be concluded that electrostatic interactions between the emulsion droplets and the porous material have a large effect on the permeability reduction. Another observation was that the porous cores did not show a uniform oil saturation. The largest oil retention was at the inlet side of the core.

3.2 Permeability of porous media

The permeability of a porous medium follows directly from Darcy's equation for the flow of a fluid through a porous medium:

\[ v_s = - \frac{K}{\eta} \nabla p = \frac{K}{\eta} \frac{\Delta p}{L} \]  

(3.1)

where \( v_s \) is the superficial fluid velocity, \( \eta \) the fluid viscosity, \( \nabla p \) the pressure gradient, \( L \) the length of the porous medium and \( K \) the permeability.

Another (empirical) equation describing the flow through porous media is the Ergun equation [8]:

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Here $\varepsilon$ is the porosity of the porous medium and $d$ the particle size of the grains of the porous core. The second term on the right hand side of 3.2 can be neglected, since this term describes the turbulent part of the flow.

Combination of 3.1 and 3.2 leads to an approximate equation for the permeability:

$$K = \frac{d^2 \varepsilon}{150(1-\varepsilon)^2}$$

(3.3)

With this equation a prediction can be made for the initial permeability of a porous medium if the grain size and the porosity are known.

### 3.3 Permeability reduction

Flow of an emulsion through a porous medium, which was initially saturated with the continuous phase of the emulsion, can result in a large permeability reduction. Two mechanisms may be responsible for this effect [6].

The most important mechanism is the straining of drops in a pore constriction. Emulsion droplets with diameters somewhat larger than the pore constriction can be captured and fully block the pore. This results in a redistribution of the flow among the neighboring pores. The permeability reduction caused by this mechanism will be very large since all the pores connected to the blocked one do not contribute to the flow of the emulsion any more. However since the drops are deformable, the drops may re-entrain in the flowing stream, if the pressure drop increases enough to overcome the capillary forces [9]. This re-entrainment can be described with the capillary number (see page 8), which is the ratio of the viscous and the capillary forces:

$$N_C = \frac{\eta v}{\gamma}$$

(3.4)
The second mechanism contributing to the permeability reduction is the interception mechanism. The emulsion droplets will be trapped in circulation eddies, or attach to pore wall due to van der Waals forces or hydrodynamical forces. This mechanism has only a small effect on the overall permeability reduction.

Both mechanisms indicate that the permeability reduction is caused by a decrease in effective porosity or free volume available for flow. The effective porosity can be written as a function of the initial clean bed porosity \( \varepsilon_0 \) and the oil or water saturation:

\[
\varepsilon_e = (1 - s) \varepsilon_0 = S \varepsilon_0
\]  
(3.5)

with \( s \) the oil saturation and \( S \) the water saturation of the porous medium. Combination of 3.5 and 3.3 gives an expression of the relative permeability (ratio of the permeability and the initial permeability) as a function of the degree of saturation:

\[
\frac{K}{K_0} = \frac{S^3 (1 - \varepsilon_0)}{(1 - S \varepsilon_0)^2}
\]  
(3.6)

This relation is only valid for a uniform saturation of the core. In practice however uniform saturation does not occur. The next section gives a description for the more practical situation, in which the saturation depends on the position in the core.

### 3.4 Non-uniform saturation of a porous medium

Experimental results of McAuliffe [2] with three parallel series of three identical cores, showed that the oil saturation near the inlet was higher than at the end of the core. This results in a relative permeability that is a function of the position in the core.

We can understand the non-uniform saturation of a porous medium as a direct result of the polydisperse character of the emulsions, if we consider that the permeability reduction is largest for high permeability media [2]. Suppose we start injecting an emulsion with particle concentration \( c_0 \) and mean particle size \( d_m \). In the first section of the core the largest particles
will be captured first, so that in the next sections, saturation with an emulsion with $c < c_0$ and $d < d_m$ will take place. At the moment the first section is completely saturated, the emulsion flowing into the second section will have the same particle size distribution as the injected emulsion. Saturation of this second section will be more difficult since it is already saturated with the emulsion with the smaller droplet size. Since the permeability reduction is largest in high permeability media, the second section will have a lower final saturation compared to the first section. The same argumentation can be applied to the third, fourth and further sections.

Darcy's equation can be written as an integration over all the sections $dx$ of the porous medium, assuming a local permeability $K(x)$:

$$v_g = \frac{\Delta P_{tot}}{\eta} \left[ \frac{L}{\int_0^L \frac{dx}{K(x)}} \right]^{-1}$$

with

$$K(x) = \frac{d^2 S(x)^3 \varepsilon_0^2}{150[1-S(x)\varepsilon_0]^2}$$

The problem is finding a suitable function $S(x)$, which is a function of the volume emulsion that has been injected in the core.

Soo [6] gives an equation for the oil saturation of the porous bed as a function of time and position for a monodisperse emulsion:

$$s = \frac{\sigma(T, \bar{x})}{\varepsilon_0} = \frac{1 - e^{\alpha \Delta s \varepsilon_0 T}}{\alpha[1 - e^{\Delta s \bar{x}} - e^{\alpha \Delta s \varepsilon_0 T}]}$$

where $\bar{x}=x/L$ is a reduced axial distance, $T = \tau - \bar{x}$ is a shifted time variable with $\tau = \frac{Qt}{V_p}$, the number of injected pore volumes emulsion. This equation assumes uniform saturation when a steady state is reached and is thus only valid for strictly monodisperse emulsions. For emulsions having a certain polydispersity the homogenous saturation will not occur.
Chapter 3

Figure 3.1 Saturation profiles with the assumptions described below. It is however not likely that the profiles are straight.

Since strictly monodisperse emulsions will not occur in practice, this equation will not have any practical importance.

A series of assumptions about the \( S(x,t) \) function can be made. First it is assumed that an instantaneous saturation of the injection plane will occur. The reason for this assumption is that as soon as the emulsion starts entering the pore, the smallest pores will be blocked, and the flow will redistribute among the other pores resulting in a higher interstitial velocity, keeping the other pores from being blocked.

The second assumption is for the end of the porous medium. It is assumed that the porous material is almost completely saturated with water here, since behind the back plane no pores are available which can be blocked. Thus no oil retention will take place here.

The saturation of a certain section of the porous medium is also a function of the volume dispersed phase which has passed the section. This can be expressed as the number of pore volumes emulsion injected \((\tau)\) times the concentration dispersed phase in the inlet \((c_i)\).

The permeability reduction proceeds faster in the first stages of the injection of emulsion. As \(c_i\) becomes larger, the rate of permeability reduction will decrease.
Transport of emulsions through porous media

3.5 Experimental

3.5.1 Emulsions

Emulsions are prepared as described in chapter 2; the total volume of each emulsion preparation was 10 litres. The concentration of the dispersed phase was 1% v/v for all experiments performed. The sodium oleate concentration was 0.5 mmol/l; if sodium chloride was added, the concentration will be named. For particle sizing the Coulter Counter was used. For the experiments performed with the Aerosol OT stabilized emulsions a surfactant concentration of 1 mmol/l was used and no sodium chloride was added.

3.5.2 Preparation of porous cores

To prepare a porous core, glass beads with a narrow size distribution were cleaned according to Eylander [10]: The glass was washed with alcoholic lye, double distilled water, hydrofluoric acid and double distilled water.
A perspex cylinder (Figure 3.2) was heated to about 80°C. At the bottom of the warm cylinder, a sintered glass filter was placed. The cylinder was filled with the cleaned glass beads, and closed with another sintered glass filter and slowly cooled to room temperature. The perspex cylinder shrinks around the filter plates, which keeps them in place. After cooling, the core could be mounted in the flow apparatus.

3.5.3 The Flow apparatus

A schematic picture of the flow apparatus is shown in figure 3.3. At the left side, two liquid containers, filled with emulsion and water respectively, are connected to the pump. The pump used was either a Verder micro gear pump or an ISCO model 2350 HPLC pump. The micro gear pump had the disadvantage that the flow rate was not constant during an experiment, but decreased as the pressure increased. From the pump the emulsion flows through the porous core. The pressure difference across the core is measured using a Validyne differential pressure transducer. At the end of the apparatus the emulsion flows into a waste beaker.
3.6 Results and discussion

3.6.1 Characterization of the porous media.

Figure 3.4 shows the particle size distributions of the glass beads used to produce the porous cores. As can be seen, two types of glass were used: 1) 10-30 µm and 2) 40-60 µm.

A segment of a core made of the 40-60 µm glass was used to measure the pore size distribution using mercury porosimetry. A porosity of 0.375 and a density of 2.810 g/cm³ were measured. The resulting pore size distribution is shown in figure 3.5. The density is in good agreement with the value measured with a Quantachrome stereopycnometer: 2.807 cm³/g.

To determine the initial clean bed permeability $K_0$, the pressure drop across the porous bed was measured, with water flowing through it at several flow rates. Plotting of this flow rate against the pressure gives a straight line according to Darcy's law (equation 3.1) with a slope $K/\eta L$. From the intercept at the $p$-axis the hydrostatic pressure across the porous...
Figure 3.5 Pore size distribution measured with mercury porosimetry of a porous medium prepared with 40-60 μm glass beads.

Figure 3.6 Determination of the initial clean bed porosity $K_0$. Intercept at $p$-axis is the hydrostatic pressure across the porous medium.
Figure 3.7 Permeability reduction of a porous medium (particles 40-60 μm) as a function of the number of pore volumes dispersed phase, measured with the micro gear pump. ▲ \( d_p = 1.75 \) μm; ● \( d_p = 8.64 \) μm \( v_s \) low; ■ \( d_p = 8.64 \) μm \( v_s \) high.

Figure 3.7 shows some permeability reductions measured with the micro gear pump. These results can be used as indicating a trend, but not for quantitative purposes, since the flow rate decreases as the pressure increases. The total permeability reduction is a function of the end saturation \( S_\infty \), which is a function of the superficial velocity. Decreasing flow rate will thus enhance the permeability reduction.

The experiments however show indeed all of the qualitative aspects of emulsion flow through a porous medium. One can observe that the final permeability reduction depends on the flow rate of the emulsion. Higher flow rates result in a lower permeability reduction. Also the influence of the particle size is shown: large particles give a larger permeability reduction then smaller ones at the same flow rate.
Figure 3.8 Permeability reduction of a porous medium (particles 40-60 μm) as a function of the number of pore volumes dispersed phase, measured with the HPLC pump. $v_s=2.21$ mm/min; • $d_p=5.1$ μm; ▲ $d_p=8.9$ μm

Figure 3.9 Permeability reduction of a porous medium (particles 40-60 μm) as a function of the number of pore volumes dispersed phase, measured with the HPLC pump. $d_p=8.9$ μm/min; ▲ $v_s=2.21$ mm/min; • $v_s=3.87$ mm/min.
Some results of the experiments with the HPLC pump are shown in figures 3.8 and 3.9. The flow rate is now constant for the duration of the experiments. The resulting final permeability reduction is smaller than the corresponding experiments with the micro gear pump. Also much more (about 10 times as much) emulsion has to be injected to reach the final permeability reduction.

Figure 3.8 shows the influence of the particle size of the emulsion. Both curves are measured at the same flow rate of 4 ml/min. The large particles give rise to a larger permeability reduction. This is quite obvious since large particles can block more pores. The particle size distributions of the inlet and effluent emulsions were the same, indicating a large repulsion between the particles and the porous material (See also 3.6.4). If the repulsion would be reduced, a change in particle size distribution of the effluent might have been observed because larger particles would be captured more easily than the smaller ones.

The effect of the superficial velocity of the emulsion is shown in figure 3.9. The emulsion had a volume average droplet diameter of 8.9 µm. For the lower flow rate, a larger permeability reduction was observed. Some drops captured at the lower flow rate will squeeze through the pore throats.

Figure 3.10 Bimodal particle size distribution of the inlet emulsion. Modal diameters are 2.0 and 5.0 µm.
Figure 3.11 Permeability reduction caused by a bimodal emulsion.

Figure 3.12 Particle size distributions of the effluent emulsions as a function of the number of injected pore volumes dispersed phase. 1) $\tau c_i=0.004$; 2) $\tau c_i=0.01$; 3) $\tau c_i=0.02$; 4) $\tau c_i=0.04$; 5) $\tau c_i=0.90$.
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3.6.3 Flow of bimodal emulsions through porous media.

As indicated in section 3.6.1, there is a large influence of the particle size on the permeability reduction. The relative permeability at the steady state decreased from 0.76 to 0.36 when the average diameter of the droplets was almost doubled from 5.1 $\mu$m to 8.9 $\mu$m.

To investigate the influence of the droplet size distribution on the permeability reduction an emulsion with a bimodal particle size distribution was injected in a porous core. Figure 3.10 shows the particle size distribution of the influent emulsion as a function of time. The two modal droplet diameters were 1.66 $\mu$m and 5.14 $\mu$m.

Figure 3.11 shows the permeability reduction of this experiment. The initial permeability was 7.0 $\mu$m$^2$. Since however the micro gear pump was used these data can be used as indicating the trend only.
The change in particle size distribution was measured with the coulter counter as a function of the number of injected pore volumes emulsion. The results are shown in figure 3.12.

Almost immediately after the emulsion started penetrating the core, particles with a small diameter were observed in the effluent. After a short time larger droplets appeared and their number increased faster than the number of small particles. When the larger particles had almost reached their final steady state value the concentration of small particles started to grow faster until finally the particle size distributions of the inlet and effluent emulsions were identical.

In figure 3.13 the relative number of particles smaller and larger then 2.8 μm are shown to illustrate the process.

3.6.4 Electrostatic repulsion and the permeability reduction

3.6.4.1 ζ-Potential of the porous medium

To investigate the influence of the sodium chloride concentration, first the ζ-potential of the porous medium was studied. The ζ-potential of the porous medium was measured with a streaming potential technique. A U-tube (figure 3.14) was filled with the glass sample and connected to a
vessel containing the solution used for the measurement. Via a series of valves and pressure regulators, this vessel could be pressurized. As pressure was applied to the vessel, the solution started flowing through the glass sample in the U-tube. The electrical potential across the sample was measured with two Ag/AgCl electrodes.

After subtracting the polarisation potentials the streaming potential for the applied pressure was obtained. With this value and assuming laminar flow through the glass sample, the $\zeta$-potential could be calculated:

$$\zeta = \frac{\eta}{\varepsilon_0 \varepsilon_r} K_{sp} \frac{E_s}{\Delta p}$$

(3.10)

Here $\eta$ is the viscosity of the solution, $K_{sp}$ the specific conductivity of the solution, $E_s$ the streaming potential and $\Delta p$ the pressure difference.

The assumption of laminar flow seemed to be a valid one. This could be concluded from experiments with sea sand at various pressure differences: the streaming potential was proportional to the applied pressure up to 1 atmosphere.

Figure 3.15 shows the $\zeta$-potential of the 40-60 $\mu$m glass beads as a function of the sodium chloride concentration at a NaOl concentration of 5 mmol/l sodium oleate at pH=10 versus the sodium chloride concentration.
Figure 3.16 ζ-potential of 40-60 μm glass beads at pH=10. [NaOl]+[NaCl]=5 mmol/l.

mmol/l and pH=10. At low salt concentrations the ζ-potential can reach rather high values, up to -100 mV for no added salt.

Figure 3.16 shows the ζ-potential of the glass beads as a function of the sodium oleate concentration. The ionic strength was kept constant by adding sodium chloride. The ζ-potential was constant over several decades of the NaOl concentration. This indicates that the glass beads are completely covered by a layer of oleate molecules. This observation was confirmed by measurement of the surface tension of the NaOl solution before and after contact with the glass. After contact the surface tension was lower, so the concentration of sodium oleate was decreased by adsorption on the glass beads. The difference in the sodium oleate concentration before and after adsorption on the glass beads was used to estimate the coverage of the glass surface. It was found that the surface concentration was about 10^{-5} mol/m^2. From this concentration a surface area per oleate molecule of 17 Å^2 was estimated.
Transport of emulsions through porous media

Figure 3.17 Influence of the electrostatic repulsion on the permeability reduction. ▲ [NaCl]=0 mol/l, \(d_p=6 \, \mu m\); ● [NaCl]=5*10^{-3} \, mol/l, \(d_p=6 \, \mu m\); ▼ [NaCl]=0.1 mol/l, \(d_p=3 \, \mu m\). Flow rate 2.5 ml/min.

3.6.4.2 ζ-Potential of the emulsion droplets.

The ζ-potential of the emulsion droplets can also reach very high values if no salt is added to the emulsion. The results of the measurements of the ζ-potentials of the emulsions are described in chapter 2.

3.6.4.3 The influence of the salt concentration on the permeability reduction.

To study the influence of the electrostatic interaction on the permeability reduction some experiments were carried out with emulsions containing sodium chloride to change the electrostatic repulsion.

Figure 3.17 shows the influence of the ζ-potential on the permeability reduction for a NaOl stabilized emulsion. The permeability reduction seemed to proceed faster if the ζ-potential is reduced by adding salt to the emulsion. The initial rate of permeability reduction for the emulsion containing 5 mmol/l was twice as large as for the emulsion without salt (Both emulsions had an average diameter of 6 \( \mu m \)). The final relative permeability was however higher.
Figure 3.18 Permeability reduction with an AOT stabilized emulsion. [$\text{[AOT]} = 1 \text{ mmol/l}; \text{flow rate } 4 \text{ ml/min}; \text{droplet diameter } 2.5 \text{ µm}.$]

Comparing the 6 µm emulsion with the 3 µm emulsion shows that at the relatively high salt concentration (0.1 mol/l) the permeability reduction is larger than at low salt concentration.

All these results indicate that the electrostatic repulsion between the emulsion drops and the porous medium plays an important role in the mechanism of the permeability reduction. From the experiments with the 6 µm emulsion (figure 3.17) it can be concluded that the drops enter the pores faster if the electrostatic repulsion is reduced. But since the repulsive force is lowered, the drops will be squeezed through the pore throats more easily. This gives the higher end permeability.

Reducing the electrostatic repulsion will also enhance the relative importance of the Van Der Waals forces, so emulsion droplets can be captured more easily in circulation eddies. Probably this is the case with the small 3 µm emulsion in figure 3.17. The permeability reduction by the small particles is larger then by the large particles. This can be a result of a domination of the interception mechanism due to the low electrostatic repulsion at the relatively high salt concentration.
It would be interesting to study the permeability reduction at even higher salt concentration but than the emulsions will not be stable enough anymore to carry out the experiments.

In the next chapter a theoretical consideration of the interaction between a spherical particle and a funnel-like pore is described.

3.6.5 Emulsions stabilized with Aerosol OT

In experiments with emulsions stabilized with Aerosol OT the emulsions all showed coalescence in the porous medium. This resulted in the formation of large oil blobs in the porous medium. The permeability reduction (figure 3.18) of the porous medium was very large, resulting in very high pressure differences. These data are in agreement with what is found in chapter 2. To investigate these processes it is again necessary to have interfacial rheological data available, to explain and predict the behaviour of the emulsion in the porous core.

3.7 References

Chapter 4

A microscopic pore model

4.1 Introduction

When stable emulsions flow through porous media, large permeability reductions can occur. A study of this phenomenon can be found in chapter 3. To elucidate the mechanism of plugging of pores, a model is presented in which the interactions between a spherical particle and a funnel-like pore throat are analyzed.

The particle in the pore will be subjected to five different forces: Attractive forces due to Van Der Waals interaction, repulsive forces due to a partial overlap of the electrical double layers of the particle and the pore wall, drag forces induced by the flow of the continuous phase around the particle, buoyancy, and capillary forces. The last two forces are ignored: it is assumed that there is no density difference between the particle and the continuous phase, and that the particle is spherical.

Figure 4.1 shows the geometry of the pore and the definition of the symbols used in this chapter.

4.2 London-van der Waals Forces.

The calculation of the attractive forces between the porous material and the spherical particle is carried out by almost the same approach Hamaker [1] used to calculate the adhesive forces between two particles. In doing so, retardation effects are neglected. To calculate the energy of attraction
Figure 4.1 Pore geometry used for the calculation of the London-Van Der Waals forces, the repulsive forces and the hydrodynamic forces.

between two bodies, containing q atoms per unit volume, the London-Van Der Waals forces must be integrated over the volume of the particle and the porous material:

$$E = - \int_{V_1} dV_1 \int_{V_2} dV_2 \frac{q^2 \lambda}{r^6}$$  \hspace{1cm} (4.1)

Here $\lambda$ is the London-Van Der Waals constant, $V_1$ and $V_2$ are the volumes of the particle and the porous material respectively, and $r$ is the distance between the volume elements $dV_1$ and $dV_2$.

The two integrals of equation 4.1 are calculated seperately. First the integration over the spherical particle (Radius $R_p$) is performed (Figure 4.2). The result is the energy of interaction between the particle and one atom of the porous material at a distance $a$ from the center of the particle:

$$E_p = - \frac{4\pi \lambda q}{3} \frac{R_p^3}{a^2 - R_p^2}$$ \hspace{1cm} (4.2)
Figure 4.2 Calculation of the interaction energy between a spherical particle and one atom.

Using this equation it is possible to calculate the complete energy of interaction. To do this we must perform the second integration of equation 4.1. This is an integration over the porous material. In all further calculations cylindrical coordinates \((r, z, \theta)\) are used. The distance \(a\) of equation 4.2 is converted to these coordinate by using the following expression:

\[
a = \sqrt{r^2 + (z-h)^2}
\]  

Substitution of equation 3 in equation 2 gives the final expression for calculating \(E_p\):

\[
E_p = -\frac{4\pi \lambda g}{3} \left[ \frac{R_p}{r^2 + (z-h)^2 - R_p^2} \right]^3
\]  

The second integration can now be carried out, using cylindrical coordinates:

\[
E_A = \int \int \int E_p \, qr \, dr \, dz \, d\theta
\]  

\[
0 \to \infty R(z)
\]  

Evaluation of this integral requires it to be split into three parts. The first integration is carried out over the upper cylindrical part (radius \(R_1\))
of the pore, the second integration over the middle, i.e. the conical part (radius \( R(z) \)), and the third over the lower cylindrical part (radius \( R_2 \)) of the pore. After integration over \( \theta \) this gives:

\[
- \frac{3E_A}{8A_{\text{Ham}}R_p^3} = \int_{-\infty}^{0} \int_{0}^{\infty} \frac{r \, dr \, dz}{R_2 \left( r^2 + (z-h)^2 - R_p^2 \right)^3} + \\
\int_{0}^{z_0} \int_{0}^{\infty} \frac{r \, dr \, dz}{R(0) \left( r^2 + (z-h)^2 - R_p^2 \right)^3} + \\
\int_{z_0}^{\infty} \int_{0}^{\infty} \frac{r \, dr \, dz}{R(z) \left( r^2 + (z-h)^2 - R_p^2 \right)^3} \tag{4.6}
\]

Here \( A_{\text{Ham}} = \lambda \pi^2 q^2 \) is the Hamaker constant and \( R(z) = R_2 + (z+h)(R_1-R_2) \). The three terms \( E_1, E_2 \) and \( E_3 \) respectively) of the right hand side of equation 4.6 can be solved using some standard integral (see appendix I). This results in 7 relevant equations to calculate the energy of attraction.

One of the first three equations can be used to calculate the part of the attraction caused by the atoms in the lower part of the pore, depending on the radius of the pore throat and the radius of the particle. To simplify the equation, we introduce: \( a = R_2^2 - R_p^2 + h^2 \), \( b = 2h \) and \( q = 4(R_2^2 - R_p^2) \). If the particle is smaller than the pore throat \( (q > 0) \) the following equation is used to calculate \( E_1 \) (see Appendix I)

\[
4E_1 = \frac{b}{qa} + \frac{2}{q\sqrt{q}} \left[ 2\arctan \frac{b}{\sqrt{q}} + \pi \right] \tag{4.7a}
\]

If the particle and the pore throat have the same radii \( (q = 0) \) the following equation is used:

\[
4E_1 = \frac{1}{3h^3} \tag{4.7b}
\]
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To calculate $E_1$ if the particle is larger than the pore throat ($q<0$), the following expression is used:

$$4E_1 = \frac{b}{qa} + \frac{2}{q\sqrt{-q}} \ln \frac{b-\sqrt{-q}}{b+\sqrt{-q}}$$

(4.7c)

To calculate the second part of the total energy of attraction, one of the following equations is used depending on the parameters $a'=R_2^2-R_p^2+h^2$, $b'=2\left[\frac{R_2(R_1-R_2)}{z_0}-h\right]$, $c'=1+\left[\frac{R_1-R_2}{z_0}\right]^2$ and $q'=4a'c'-b'^2$.

If $q'>0$ then the following equation is used:

$$4E_2 = \frac{2c'z_0+b'}{q'Z_0} - \frac{b'}{q'a'} + \frac{4c'}{q'\sqrt{-q'}} \left[ \arctan \frac{2c'z_0+b'}{\sqrt{-q'}} - \arctan \frac{b'}{\sqrt{-q'}} \right]$$

(4.8a)

Here $Z_0=a'+b'z_0+c'z_0^2$, according to appendix I.

For $q'=0$ the following expression is applied to calculate $E_2$:

$$4E_2 = \frac{8c'}{3b'^2} - \frac{1}{3c^2\left(z_0+\frac{b'}{2c'}\right)}$$

(4.8b)

If $q'<0$

$$4E_2 = \frac{2c'z_0+b'}{q'Z_0} - \frac{b'}{q'a'} + \frac{4c'}{q'\sqrt{-q'}} *$$

$$\left[ \ln \frac{2c'z_0+b'-\sqrt{-q'}}{2c'z_0+b'+\sqrt{-q'}} - \ln \frac{b'-\sqrt{-q'}}{b'+\sqrt{-q'}} \right]$$

(4.8c)

For the calculation of $E_3$ only the solution for $R_1>R_p$ is relevant ($a''=R_1^2-R_p^2+h^2$, $b''=-2h$ and $q''=4\left(R_1^2-R_p^2\right)$):

$$4E_3 = \frac{2z_0+b''}{q''Z_0} + \frac{2}{q''\sqrt{q''}} \left[ \pi - 2\arctan \frac{2z_0+b''}{\sqrt{q''}} \right]$$

(4.9)

The total energy of attraction can now be calculated by adding $E_1$, $E_2$ and $E_3$. With this result the attractive force which the particle experiences
Figure 4.3 Calculation of the total repulsive force by dividing the particle in an odd number of slices.

is easily derived by differentiating the energy of attraction with respect to the height of the particle in the pore:

\[ F_A(h) = -\frac{\partial E_A(h)}{\partial h} \] (4.10)

A computer program has been written to evaluate equations 4.7 to 4.10.

4.3 Electrostatic repulsion

To calculate the electrostatic repulsion between a particle and the pore, an equation is derived for the electric potential in a cylindrical gap. Dividing the particle into cylindrical slices (Figure 4.3) and summing the interaction of those slices gives then the total interactive force.

4.3.1 Electrical double layer interaction in a cylindrical gap.

The electrical double layer interaction in a cylindrical gap is calculated by integrating the Poisson-Boltzman [2] equation using cylindrical coordinates. This solution gives the electrical potential as a function of the position in the gap. Using the minimum in this curve, the osmotic pressure
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in the gap can be calculated. According to Langmuir [3] the osmotic pressure can then be used to calculate the repulsive force.

To integrate the Poisson-Boltzmann equation we start at the general equation:

\[ \nabla^2 \Psi = -\frac{\rho}{\varepsilon_0 \varepsilon_r} \tag{4.11} \]

In this equation \( \rho \) is the volume charge density, which can be calculated from the concentration of ions in the bulk solution, \( \Psi \) the potential function and \( \varepsilon \) the dielectric constant. The volume charge density is given by:

\[ \rho = -2z_\pm e_0 n_0 \sinh \frac{z_\pm e_0 \Psi}{kT} \tag{4.12} \]

where \( e_0 \) is the charge of an electron, \( n_0 \) the number of ions per volume, and \( z_\pm \) the valency of the ions.

Because of the cylindrical symmetry the terms in \( \theta \) and \( z \) disappear in the expansion of the \( \nabla^2 \) operator. Equation 4.11 then becomes:

\[ \frac{\partial^2 \Psi}{\partial r^2} + \frac{1}{r} \frac{\partial \Psi}{\partial r} = 2z_\pm e_0 n_0 \sinh \frac{z_\pm e_0 \Psi}{kT} \tag{4.13} \]

To solve this equation, it is made dimensionless by defining the following parameters:

\[ y = \frac{z_\pm e_0 \Psi}{kT}, \quad \alpha = \frac{z_\pm e_0}{kT}, \quad \text{and} \quad x = \kappa (r - R_p) \]

where \( R_p \) is the radius of the inner cylinder. The parameter \( \kappa \) is the reciprocal Debye-length of the electrical double layer:

\[ \kappa^2 = \frac{2z_\pm e_0^2 n_0}{\varepsilon_0 \varepsilon_r kT} \tag{4.14} \]

The dimensionless equation is scaled by defining \( x = \beta t = \kappa (R - R_p) t \) resulting in the final differential equation suitable for numerical solution:

\[ \frac{d^2 y}{dr^2} + \frac{\alpha \beta}{\beta t + \kappa R_p} \frac{dy}{dt} - \beta^2 \sinh y = 0 \tag{4.15} \]
This equation was solved using a finite difference relaxation scheme (NAG-library subroutine D02GAF) (An initial solution is guessed that approximately satisfies the differential equation and boundary conditions. An iterative process adjusts the function to bring it into close agreement with the true solution). In so doing a specified surface potential on the inner and outer surface of the cylindrical gap was used. A typical solution of equation 4.15 is shown in figure 4.4. Due to the diverging term, i.e. \( \frac{1}{r} \left( \frac{\partial \psi}{\partial r} \right) \), in the Poisson-Boltzmann equation, the minimum in the curve is not in the middle of the gap, but somewhere near the inner boundary.

4.3.2 The repulsion between the particle and the pore

The total repulsive force between the particle and the pore is calculated by dividing the particle in an odd number of horizontal slices as shown in figure 4.4. For each slice the potential curve was calculated as described in the previous paragraph. The minimum in the potential was used to calculate the osmotic pressure using the Langmuir equation [3]:

\[
p = 2n_0 kT (\cosh \gamma_{\text{min}} - 1)
\]

(4.16)
Multiplying this pressure with the surface area of the slice, its contribution to the total repulsive force can be calculated:

\[ F_R = \sum_{i=1}^{n_{\text{slice}}} \pi R_{\text{slice},i} p_i \sin 2\theta_i \Delta z \]  

(4.17)

where \( \Delta z \) is the height of a slice, \( R_{\text{slice},i} \) is the radius of the slice and \( \theta_i \) is the angle between direction of the osmotic pressure (i.e. the direction of the \( r \)-axis) and the normal of the particle surface.

4.4 Hydrodynamic force

To calculate the hydrodynamic drag forces caused by the flow of the continuous phase, the Navier-Stokes equation [4] together with the continuity equation must be solved. The solution was obtained by using the Finite Element Method with the Penalty Function Approach [4]. The resulting velocity profile was used to calculate the drag coefficient.

4.4.1 The Navier-Stokes equations

To calculate the velocity profile of the continuous phase cylindrical coordinates \((r,z,\theta)\) are used. The equations governing the flow are the continuity equation, which is in fact a mass balance for a small volume element of fluid

\[ \nabla \cdot \mathbf{u} = 0 \]  

(4.18)

and the Navier-Stokes equation:

\[ -\eta \nabla^2 \mathbf{u} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = \rho \mathbf{f} \]  

(4.19)

Here \( \mathbf{u} \) is the velocity of the fluid phase, \( p \) is the pressure, which is known up to a constant, and \( \mathbf{f} \) are external forces acting on a volume element.

By introducing a characteristic length \( L \) and a characteristic scalar velocity \( U_0 \), and using the following definitions these equations can be written dimensionless.
Figure 4.5 Domain and boundary conditions for the calculation of the hydrodynamic force acting on a particle in a funnel-like pore.

\[ x' = \frac{x}{L}, u' = \frac{u}{U_0}, p' = \frac{p}{\rho U_0^2} \text{ and } f' = \frac{f}{\nu^2 L} \]

Omitting the primes, we obtain:

\[ \nabla u = 0 \] (4.20)

and

\[ -\frac{1}{Re} \Delta u + (u \nabla)u + \nabla p = f \] (4.21)

where Re is Reynolds number defined by \[ Re = \frac{\rho U_0 L}{\eta} \].

In the specific case of the funnel-like pore studied in this chapter the characteristic length is chosen to be equal to the particle diameter. At the inlet of the pore a parabolic velocity profile is assumed. The characteristic velocity \( U_0 \) is defined as the maximum of this parabolic profile.

Since we are dealing with low Reynolds numbers (laminar flow), the non-linear convective terms can be neglected, transforming equation 4.21 into the Stokes equation. In the program used for the calculations
presented below, this term is not neglected, resulting in some extra accuracy in the solution of the equations.

The pore is axisymmetric with the $z$-axis as symmetry axis. This symmetry yields that the derivates of the velocity with respect to the coordinate $\theta$ are zero and we assume also $u_\theta$ to be zero. Hence only half of the $(r,z)$ plane needs to be considered.

Figure 4.5 shows the half pore together with the boundary conditions. No slip boundary conditions ($u_r=0$, $u_z=0$) are assumed at the pore wall (boundaries 2,3,4) and the particle surface (boundary 7). The inlet velocity profile (boundary 1) can be described with the following (dimensionless) equation:

$$u_z = \left[ \frac{R_2}{R_1} \right]^2 - 1, \ u_r = 0$$ (4.22)

To prevent oscillations in the solution, Neumann boundary conditions [4] are used at the outlet of the pore (boundary 5):

$$u_r = 0, \ \frac{\partial u_z}{\partial z} = 0$$ (4.23)

Because of the axial symmetry the following boundary condition holds for the $z$-axis:

$$u_r = 0, \ \frac{\partial u_z}{\partial r} = 0$$ (4.24)

The boundary condition for the pressure is $p=0$ at the outlet of the pore.

4.4.2 The Finite Element Method

The Finite Element Method is a numerical method to solve partial differential equations on a given domain with prescribed boundary conditions. The solution of the differential equation can be written as a linear combination of an infinite series of base functions. Restriction of this series to a finite number leads to the construction of an approximate solution of the differential equation.
The region on which the approximate solution has to be calculated is divided into a number of small subdomains, called elements. Elements never may show an overlap and must, when joined together, cover the whole domain. The result is called a mesh.

The unknown velocity and pressure components on each element must now be expressed in terms of interpolation functions (polynomials). These polynomials \( \varphi_j \) and \( \psi_j \) are chosen such that they are continuous on the domain and have a prescribed behaviour for every element (e.g. linear or quadratic). For the base functions also the relations \( \varphi_j(x_i) = \delta_{ij} \) and \( \psi_j(x_i) = \delta_{ij} \) must be satisfied.

The element used here is a 7-noded \((P2+,P1)\) modified triangular Crouzeix-Raviart element [4] (Figure 4.6). The velocity is expressed with quadratic polynomials as base function, using seven nodal points to define them, whereas the pressure for this element is expressed by linear polynomials, defined by one nodal point and two derivatives.

To solve the Navier-Stokes equation, the convective term must be linearized. This can be done by a Newton iteration scheme:

\[
(u^i \cdot \nabla) u^i = (u^{i-1} \cdot \nabla) u^i + (u^i \cdot \nabla) u^{i-1} - (u^{i-1} \cdot \nabla) u^{i-1}
\]  

(4.25)
Substitution of this equation in the Navier-Stokes equation gives for the i-th iteration:

\[- \frac{1}{\text{Re}} \Delta u^i + (u^{i} \cdot \nabla) u^{i-1} + (u^{i-1} \cdot \nabla) u^i + \nabla p^i = (u^{i-1} \cdot \nabla) u^{i-1}\]

(4.26)

\[(\nabla \cdot u^i) = 0\]

(4.27)

To make the solving easier the principle of the Penalty Function Approach is applied. This means that the equation of continuity is perturbed. This perturbation can be considered as an introduction of a slight artificial compressibility of the fluid.

\[\nabla u = - \frac{1}{\tau} p\]

(4.28)

The parameter \(\tau\) is called the penalty-function parameter and has a large value. This approximation can be justified because the continuity equation is satisfied for \(\tau \to \infty\), due to the finite value of the pressure. Furthermore, equation 4.28 is not in contradiction with the boundary conditions.

Substitution of the interpolation functions \(\varphi_j(r,z)\) and \(\psi_j(r,z)\) in equations 4.26 and 4.28 gives a set of linear equations, called the Galerkin equations:

\[S U^i + N(U^i) U^{i-1} + N(U^{i-1}) U^i + \tau L^T D^{-1} L U^i = N(U^{i-1}) U^{i-1}\]

(4.29)

\[P^i = \tau D^{-1} L U^i\]

(4.30)

In this equation \(D\) is the pressure matrix, a discretization of the pressure in the system. The matrix \(L\) contains terms due to the discretization of the divergence operator \((\nabla)\). In \(N\) the discretized convective terms of the Navier-Stokes equation can be found, and in \(S\) the diffusion terms. The vector \(U\) contains the unknown velocities in the nodal points for the velocity (seven per element) and \(P\) the unknown pressure parameters in the nodal points (one per element) for the pressure. This set of equations can be solved numerically in an efficient way. As initial solution for the Newton iteration, the solution of the Stokes equation is used.

The calculations where terminated if

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Figure 4.7 Definition of the angle θ used for calculating the drag coefficient.

\[
\|\mathbf{u}^i - \mathbf{u}^{i-1}\| < 10^{-4}
\]  (4.31)

The advantage of the penalty function approach is mainly that the pressure is eliminated from the momentum equations, resulting in a set of equations that can be solved without partial pivoting (i.e. decomposition of the system matrix in an upper triangular and lower triangular matrix). Hence a substantial decrease in computer time and memory is saved compared to direct solution of the unperturbed continuity equation. The solution of the velocity profile is entirely determined by equation 4.29. After solving this equation the pressure profile can be calculated by applying equation 4.30, which is essentially a differentiation of the velocity profile.

The disadvantage of the penalty function approach is that the parameter τ must be chosen carefully, since otherwise loss of accuracy may occur due to the singularity of the resulting matrix. Practical values for τ are in the range such that \( \frac{D}{\tau} = 10^{-6} \)

### 4.4.3 Calculation of the drag force

To calculate the drag force or the drag coefficient the vertical z-components of the normal and tangential stress at the particle surface need to
be integrated over the particle surface [5]. The normal stress will be formed by the hydrodynamic pressure and the tangential stress is equal to the vorticity at the particle surface. This leads to the following equation to calculate the drag coefficient:

\[
C_d = \frac{F}{0.5 \rho AU^2} = -2 \int_0^\pi p_x \sin 2\theta \, d\theta - \frac{4}{Re} \int_0^\pi \xi_2 \sin^2 \theta \, d\theta \tag{4.32}
\]

Here \( F \) is the drag force acting on the sphere, \( A = \pi R_p^2 \) is the area of the sphere, \( \theta \) is defined as shown in figure 4.7 and \( \xi = \nabla \times u \).

4.5 Results and discussion

4.5.1 London-Van Der Waals attraction.

Figure 4.8 shows the results of the attractive force as a function of the particle size. At high positions in the pore the force decreases towards zero. This is what is expected, since the forces acting on the particle are then nearly symmetric and thus compensate each other. When the particle is descending the attractive force increases, since the distance between the particle and the pore material decreases. For particles larger than the pore throat the calculation is terminated just before the particle would contact the pore wall to prevent that the force would grow to infinity. For particles smaller than the pore throat, a maximum in the force is observed slightly above the pore throat. When the particle has entered the lower part of the pore the contribution of the middle part of the pore to the attractive force decreases and again a symmetric situation is experienced by the particle. Hence the force in the lower part of the pore will tend towards zero.

In figure 4.9 the attractive force is shown for different pore geometries. The lower and upper pore radius (\( R_2 \) and \( R_1 \) respectively) as well as the particle radius (\( R_p \)) were kept constant whereas the pore height \( z_0 \) was varied. The first fact that attracts attention is that the maximum almost shows no dependence on the pore geometry. Obviously the attractive force
Chapter 4

Figure 4.8 Attractive force calculated for different particle radii. \( A_{ham}=2.5 \times 10^{-21} \), \( R_1=5 \mu m \), \( R_2=1 \mu m \), \( z_0=14 \mu m \). 1) \( R_p=0.75 \mu m \), 2) \( R_p=0.95 \mu m \), 3) \( R_p=1.5 \mu m \), 4) \( R_p=2 \mu m \) 5) \( R_p=3 \mu m \).

Figure 4.9 Attractive force calculated for different pore heights. \( A_{ham}=2.5 \times 10^{-21} \), \( R_1=5 \mu m \), \( R_2=1 \text{mm} \), \( R_p=0.95 \mu m \). 1) \( z_0=3 \mu m \), 2) \( z_0=5 \mu m \), 3) \( z_0=7 \mu m \), 4) \( z_0=9 \mu m \) 5) \( z_0=11 \mu m \), 6) \( z_0=13 \mu m \)
Figure 4.10 An explanation of the behaviour of the Van Der Waals attractive forces. See text.

is determined by the interaction between the particle and the pore material in the neighbourhood of the pore throat.

The second fact that is observed is that the attraction at a certain positive height is larger if the pore height $z_0$ is large. Below the pore neck the attraction is larger if the pore height is small.

To explain these results, a plane of symmetry $AB$ is thought through the centre of the particle, perpendicular to the $z$-axis. If the pore would be a straight cylinder, equal amounts of material would be above and below the plane $AB$ (Figure 4.10 A). The net attractive force experienced by the particle would be zero in this case. If there was a narrowing in the pore (figure 4.10 B) than there would be more material below the plane $AB$ than above it. The amount of material below the plane $AB$ depends on the pore height $z_0$. If $z_0$ is large there is more material below the plane $AB$ then if $z_0$ small. This results in a larger net attraction for large pore heights.

If the particle descends into the lower part of the pore, there is more material below plane $AB$ too. However the amount of material above the plane now depends on the pore height (Figure 4.10 C). If the pore height is larger, more material is found above plane $AB$, resulting in a lower net attractive force for large values of $z_0$. 
4.5.2 Electrostatic repulsion

Figure 4.11 shows the influence of the number of slices the particle is divided into, on the calculated repulsive force. The curves for $n_{\text{slice}}=31$ and $n_{\text{slice}}=63$ almost coincide. Changing $n_{\text{slice}}$ to even higher values had no significant effect on the calculated repulsive force. All further calculations were performed with a value $n_{\text{slice}}=31$.

The effect of the particle size on the repulsive force is shown in figure 4.12. The values of the surface potential are chosen, such that they are in agreement with the experiments in chapter 3, where no sodium chloride was added to the emulsion. Comparing these results with the results of the attractive force calculations, it immediately appears that the repulsive forces act on a much shorter distance. Moreover, the repulsive forces are much larger, up to 4 or 5 orders difference. The electrostatic repulsion for the particles with $R_p>R_2$ has the same magnitude; as soon as the particle approaches its lowest possible position in the pore, the value of the reciprocal Debije length times the distance between the surface of the pore and the surface of the particle have the same magnitude.
Figure 4.12 The influence of the particle radius on the calculated repulsive force. $R_1=5\ \mu m$, $R_2=1\ \mu m$, $z_0=14\ \mu m$, $\Psi_0=\Psi_p=-80\ mV$, $c=0.5\ mmol/l$.  
1: $R_p=0.95\ \mu m$; 2: $R_p=1\ \mu m$; 3: $R_p=2\ \mu m$; 4: $R_p=3\ \mu m$.

Figure 4.13 The influence of the pore height on the calculated repulsive force. $R_1=5\ \mu m$, $R_2=1\ \mu m$, $R_p=0.95\ \mu m$, $\Psi_0=\Psi_p=-80\ mV$, $c=0.5\ mmol/l$.  
1: $z_0=5\ \mu m$; 2: $z_0=7\ \mu m$; 3: $z_0=9\ \mu m$; 4: $z_0=11\ \mu m$; 5: $z_0=13\ \mu m$.
Figure 4.13 summarizes the results for a series of different pore geometries for a particle smaller than the pore throat. The repulsive force has only significant values if the particle is positioned less than half its radius from the pore neck (z=0). There is only little influence of the pore height on the results on logarithmic scale. The repulsive force is somewhat larger for the higher pore narrowings. This can be explained by the fact that more slices of the particle contribute to the force. If the particle has entered the pore throat, the repulsion decreases faster for a higher pore narrowing. This can be ascribed to the same effect: more slices in the upper region of the particle play a role in the determinations of the force. However, their resulting force is now directed toward the negative z-axis, which gives the faster decrease of the total repulsion.

4.5.3 Hydrodynamic force

To check the results of the program used for calculating the hydrodynamic forces, first a solution of the Stokes problem of a sphere in a uniform flow field was calculated and compared to the theoretical values. At low Reynolds numbers the drag coefficient has a value of $C_D = 0.4\Re$.
Figure 4.15 The hydrodynamic force acting on a particle. $R_1=5 \, \mu m$, $R_2=1 \, \mu m$, $z_0=14 \, \mu m$. ▲ $R_p=0.95 \, \mu m$; ● $R_p=2 \, \mu m$.

Figure 4.14 shows the results of the calculated drag coefficient and the theoretical values. The calculated values are in good agreement with the theoretical ones. From these results it is concluded that the procedures described above can be applied for the problem of the funnel-like pore.

The results of the hydrodynamic force calculation are shown in figure 4.15. For the particle smaller then the pore throat, the drag increases to a maximum and then decreases. At large distances from the pore throat the drag will level off to a constant value.

For the large particle the drag also increases. Unfortunately was it impossible to calculate the behaviour of the particle near the lowest possible value of the particle in the pore. Here the system of equations for solving the Navier-Stokes equation became singular.

4.5.4 The total force

Figure 4.16 and 4.17 show the attractive force, the repulsive force and the hydrodynamic force in one graph. Both, the large particle and the small particle show a much larger drag force than the colloidal force. According to these graphs the particles the small particles will slip through the pore.
Figure 4.16 Attractive (▲), repulsive (●), hydrodynamic (▼) forces as function of the position of the particle. $R_1=5 \, \mu m$, $R_2=1 \, \mu m$, $z_0=14 \, \mu m$, $R_p=0.95 \, \mu m$.

Figure 4.17 Attractive (▲), repulsive (●), hydrodynamic (▼) forces as function of the position of the particle. $R_1=5 \, \mu m$, $R_2=1 \, \mu m$, $z_0=14 \, \mu m$, $R_p=0.95 \, \mu m$. 
throat. The large particles will go down further into the pore narrowing and will probably show a deformation (figure 4.18).

As the particle deforms, this will result in a much larger colloidal interaction between the particle and the pore wall, since the surface where interaction can take place will be larger and the distance between the particle and the pore will be smaller. Additionally, if deformation occurs, capillary forces start to play a role, resulting in a net force opposing the hydrodynamic drag. The deformation and the capillary force probably prevent the particle from being squeezed through the pore neck in certain situations.

To give a prediction of the total force acting on a deformed particle, more calculations are required.

4.6 References

Chapter 4


Appendix I. Standard integrals used to calculate the energy of attraction.

- Integration of equation 4.5

\[
\int \frac{r \, dr}{(r^2 + a^2)^3} = -\frac{1}{4(r^2 + a^2)^2} + C \tag{A.1}
\]

- Integration of equation 4.6.

First the integration over \(dr\) is carried out (only the first term is shown), resulting in

\[
\int_0^\infty \int_{-\infty}^{\infty} \frac{r \, dr \, dz}{(r^2 + (z - h)^2 - R_p^2)^3} = -\frac{1}{4} \int_{-\infty}^{0} \frac{dz}{(R_p^2 + (z-h)^2 - R_p^2)^2} =
\]

\[
-\frac{1}{4} \int_{-\infty}^{0} \frac{dz}{(z^2 - 2hz + R_p^2 - R_p^2 + h^2)^2} \tag{A.2}
\]

Defining \(X = a + bx + cx^2\), and \(q = 4ac - b^2\) (in case of equation A.2: \(c=1, b = -2h, a = R_p^2 - R_p^2 + h^2\) and \(q = 4(R_p^2 - R_p^2)\)):

\[
\int \frac{dx}{X^2} = \frac{2cx + b}{qX} + \frac{2c}{q} \int \frac{dx}{X} + C \tag{A.3}
\]

This result can be found by partial integration. The integral on the right hand side of equation A.3 must be solved with one of the following three standard integrals, depending on the value of \(q\).

If \(q<0\):

\[
\int \frac{dx}{X} = \frac{1}{\sqrt{-q}} \ln \frac{2cx + b - \sqrt{-q}}{2cx + b + \sqrt{-q}} + C \tag{A.4}
\]
if \( q=0 \)

\[
\int \frac{dx}{X} = -\frac{1}{3c^2(x + \frac{b}{2c})^3} + C
\]  

(A.5)

if \( q>0 \)

\[
\int \frac{dx}{X} = \frac{2}{\sqrt{q}} \arctan \left( \frac{2cx + b}{\sqrt{q}} \right) + C
\]  

(A.6)
Chapter 5

Interfacial Rheology

5.1 Introduction

When considering stability of emulsions or the behavior of emulsion droplets in porous media, one always assumes that the interfacial tension has its equilibrium value. However, since all these processes are dynamical, it is unlikely that equilibrium will exist.

As was seen in chapter 2, it is necessary to measure the interfacial rheological parameters to describe the difference in behaviour of the sodium oleate stabilized emulsion and the Aerosol OT stabilized emulsions, when coagulation is considered. In chapter 3 the importance of such parameters was seen for describing the flow of the emulsions through the porous media.

The most important parameter describing the dynamic behavior of the interface is the Gibbs elasticity modulus:

\[ \varepsilon = \frac{d\gamma}{d \ln A} \]  \hspace{1cm} (5.1)

Here \( \gamma \) is the interfacial tension and \( A \) the area of a surface element.

When values of this modulus are known as function of the frequency, predictions can be made about Marangoni effects. The modulus determines the resistance to the creation of interfacial tension gradients, as well as the speed with which such gradients dissipate. The higher the Gibbs modulus, the more rapidly the interfacial tension will be restored [1].
Perfect elastic behavior of a surface is found only when no relaxation processes occur with a characteristic time comparable with the time scale of the experiment. Such relaxation process can for instance be restoring of the adsorption gradients at the interface by diffusion of the surfactant from the bulk solution.

If relaxation processes of this kind play a role, the interface shows visco-elastic behaviour. The Gibbs modulus can then be expressed as a complex modulus, with the real part describing the interfacial dilational elasticity and the imaginary part the interfacial dilational viscosity:

\[ \varepsilon = |\varepsilon| e^{i\theta} \]  
(5.2)

with \( \theta \) the loss angle.

The interfacial dilational viscosity, which accounts for the energy dissipation in the surface, can than be expressed as:

\[ \eta_d = \frac{|\varepsilon| \sin \theta}{\omega} \]  
(5.3)

This chapter describes a technique to measure the complex modulus. A method is used analogous to the method of Lucassen and Van Den Tempel [1] except that here a Langmuir trough with two barriers moving in counterphase was used. Unfortunately, due to instrumental problems, real measurements concerning the emulsions studied in this thesis could not be performed. However the results in this chapter are promising good results if these problems will be solved.

5.2 Theory

5.2.1 Surface waves

All methods to measure the dynamic interfacial properties make use of surface waves. Two types of surface waves are known [2]:

- Ripples in the surface. The surface tension determines the curvature of the ripples. This kind of waves are also known as capillary waves and have a typical frequency in the magnitude of 100 or more Hertz.
• Longitudinal waves. These waves are comparable with sound waves: Surface active components will be periodically compressed and dilated. As a result of this periodically changing surface excess, the interfacial tension will also vary with the same frequency.

5.2.2 Longitudinal waves

In the experiments described below, a harmonic longitudinal wave will be created by two barriers positioned at the interface between two fluid phases. Both barriers move sinusoidal and in counterphase. Exactly in the middle between both barriers, the interfacial tension will be measured using a Wilhelmy plate. Figure 5.1 shows the experimental setup of the Langmuir trough and defines some of the symbols used in the rest of this chapter.

The movement of the barriers can be described by

$$\xi_I' = -\xi_{II} = \xi_B e^{i\omega t} \quad (5.4)$$

where $\xi_B$ is the amplitude of the barriers, $\omega$ is the angular velocity and $t$ is the time variable.
At a position \( x \) in the trough, the surface dilation can be described by the primary wave and a series of reflections against the opposing barrier and the generating barrier:

\[
\xi_0 = \xi_B e^{i\omega t} e^{-ikx'} \\
\xi_1 = \xi_B e^{i\omega t} e^{-ik(4x_0 - x')} e^{ip} \\
\xi_2 = \xi_B e^{i\omega t} e^{-ik(4x_0 + x')} e^{2ip} \\
\xi_3 = \xi_B e^{i\omega t} e^{-ik(8x_0 - x')} e^{3ip} \\
\xi_4 = \xi_B e^{i\omega t} e^{-ik(8x_0 + x')} e^{4ip} \\
\vdots \\
\xi_n = \xi_B e^{i\omega t} e^{-ik(4(n+1)x_0 - x')} e^{nip} \quad (n \text{ odd}) \\
\xi_n = \xi_B e^{i\omega t} e^{-ik(4nx_0 + x')} e^{nip} \quad (n \text{ even}) \\
\vdots
\]

Here \( x' = x + x_0 \), \( x_0 \) is the distance between the centre of the trough and the position of the barrier at rest, \( \phi \) the phase difference on reflection, and \( k \) is the complex wave number, describing the wave length and the damping coefficient.

The movement of the interface due to a wave generated by barrier I can be expressed as the sum of the primary wave and all its reflections. The summing is simplified by adding all terms for even \( n \) and all terms for odd \( n \):

\[
\xi_x = \sum_{i=0}^{\infty} \xi_{2i} + \sum_{j=0}^{\infty} \xi_{2j+1} \\
\]

Both terms on the right hand side are geometric series and can be expressed as a single term:
In an analogous way, defining $x'' = x_0 - x$ an equation can be derived for the deformation of the surface due to the second barrier movement:

$$
\xi''_x = \xi_B e^{i2\omega} \left[ \frac{e^{-ikx''} + e^{i(\varphi - k(4x_0 - x'))}}{1 - e^{2i(\varphi - 2kx_0)}} \right] (5.10)
$$

Adding 5.9 and 5.10 gives in combination with 5.4 a relation for the reflection angle:

$$
e^{i\varphi} = -1 (5.11)
$$

This means that the phase difference is 180° and that no damping occurs on reflection.

Using this expression the total dilation of the surface at position $x$ in the trough becomes after some rearrangements:

$$
\xi_x = \xi_B e^{i2\omega} \left[ \frac{\sin k(x_0 - x) - \sin k(x_0 + x)}{\sin 2kx_0} \right] (5.12)
$$

Further simplification of this equation gives:

$$
\xi_x = -\xi_B e^{i2\omega} \frac{\sin kx}{\sin kx_0} (5.13)
$$

With use of this equation an expression for the relative surface dilation can be found:

$$
\frac{\Delta A}{A} = \frac{\partial \xi_x}{\partial x} = -\xi_B k e^{i2\omega} \cos kx \frac{\sin kx}{\sin kx_0} (5.14)
$$

Together with the definition of the Gibbs elasticity (5.1), equation 5.14 relates the surface dilation and the interfacial tension variations:

$$
\Delta \gamma = \varepsilon \frac{\Delta A}{A} (5.15)
$$
If a uniform compression and dilation of the interface is assumed, the relative interfacial dilation is related by

\[
\left( \frac{\Delta A}{A} \right)_{\mu} = -\frac{5B e^{j\omega t}}{x_0} \tag{5.16}
\]

since \( \Delta A = 2b_0^2 e^{j\omega t} \) and \( A = 2bx_0 \) (where \( b \) is the width of the Langmuir trough).

The ratio of the interfacial tension changes due to the exact dilation and the uniform dilation can be expressed as by combination of equations 5.14 and 5.16 together with 5.15

\[
\frac{\Delta \gamma}{\Delta \gamma_u} = \frac{kx_0 \cos kx}{\sin kx_0} \tag{5.17}
\]

The complex wave number \( k \) is defined as \( k = \kappa - i\beta \), with \( \kappa \) the real wave number and \( \beta \) the damping coefficient. The last two parameters can be related to the Gibbs elasticity by [2,3]

\[
\kappa = \frac{2\pi}{\lambda} = i e^{-1/2} \omega \sqrt{\frac{\gamma}{\sqrt{\eta \rho} + \sqrt{\eta' \rho'}}} \left( \frac{\pi + \theta}{2} \right) \cos \left( \frac{\pi + \theta}{2} \right) \tag{5.18}
\]

\[
\beta = i e^{-1/2} \omega \sqrt{\frac{\gamma}{\sqrt{\eta \rho} + \sqrt{\eta' \rho'}}} \left( \frac{\pi + \theta}{2} \right) \sin \left( \frac{\pi + \theta}{2} \right) \tag{5.19}
\]

Defining the following dimensionless variables

\[
W = (\beta x_0)^{-1}, \quad D = \frac{x}{x_0} \quad \text{and} \quad B = \cot \left( \frac{\pi + \theta}{2} \right) - i \tag{5.20}
\]

equation 5.17 can be transformed into

\[
\frac{\Delta \gamma}{\Delta \gamma_u} = \frac{B}{W} \cos \frac{BD}{W} \quad \frac{B}{W} \sin \frac{B}{W} \tag{5.21}
\]

Since the interfacial tension is always measured in the centre of the trough \( (D=0) \), this equation can be simplified to
Figure 5.2 Absolute value of the ratio of the interfacial tension changes from the exact solution and the solution for uniform surface dilation as a function of the dimensionless distance from between the Wilhelmy plate and the barriers. Loss angles: 0°, 30°, 45°, 60° and 90°.

\[
\frac{\Delta \gamma}{\Delta \gamma_u} = \frac{B}{W} \sin \frac{B}{W}
\]  

(5.22)

and this can be written as

\[
\frac{\Delta \gamma}{\Delta \gamma_u} = Se^{i\delta}
\]

(5.23)

Figure 5.2 shows a plot of $S$ versus $W$ on logarithmic scale for a series of loss angles. Figure 5.3 shows a graph of $\delta$ against $W$. For values of $W$ above 4, the value of $S$ goes to unity and $\delta$ goes to 0°. This means that the deformation of the interface can be approximated as uniform. In this situation the damping of the wave can be neglected and the reflections all have a large contribution to the deformation of the surface.
Figure 5.3 Argument of the ratio of the interfacial tension changes from the exact solution and the solution for uniform surface dilation as a function of the dimensionless distance from between the Wilhelmy plate and the barriers. Loss angles: 0°, 30°, 45°, 60° and 90°.

The value of $W=4$ can be translated to the condition $x_0 < 0.25 \pi$. Hence if we make $x_0$ small enough, the Gibbs elasticity can be simply calculated using equation 5.2 and 5.15:

$$|\xi| = \frac{|\Delta \gamma x_0|}{\xi_0}$$  \hspace{1cm} (5.22)

The loss angle $\theta$ can be determined as the phase difference between the barrier movement and the measured interfacial tension.

5.3 Experimental

All experiments were performed in a Langmuir trough, made of steel, and coated with PVDF (Polyvinylidifluoroethylene). The barriers made of a thin Platinum-Rhodium wire were driven by a loudspeaker. The input
signal for the barriers was generated with an Exact model 7060 wave generator.

The interfacial tensions were measured using a platinated Wilhelmy plate, connected to a CI Electronic electrobalance.

The signal of balance was analyzed with a Solartron digital TFA JM 1600A Fourier analyser with a Solartron mechanical reference synchroniser JX 1606. The input signal to the loudspeakers was used as the reference signal.

The displacement of the barriers was measured using a Sangamo Slummberger DF5 displacement transducer.

All experiments were performed at room temperature with sodium dodecylsulphate (Merck, pro analysi) solutions in doubly distilled water.

5.4 Results and discussion

To determine the influence of the SDS concentration on the measured signal, the interfacial tension fluctuations were measured for a series of SDS concentrations. Figure 5.4 shows the signal of the balance as a function of the SDS concentration. In general, the signal decreases as the SDS concentration increases.
concentration increased. This can be explained by a growing surface occupation by the surfactant which opposes the surface compression and dilation. For the concentration of 10 mmolar (above the CMC) the signal completely disappears. The surface is than completely occupied with the surfactant. The best signal was found at 1 mmol/l. All further experiments were performed at this concentration.

To determine the surface rheological properties of the air/SDS-solution surface, interfacial tension fluctuations were measured for a number of frequencies and values of \( \lambda_0 \). Figure 5.5 shows the absolute values of the interfacial tension fluctuations as a function of the reciprocal distance between the barriers and the Wilhelmy plate. All curves are straight lines, from which it can be concluded that the approximation of uniform surface deformation may be applied. The slope of these lines gives the Gibbs elasticity.

Figure 5.6 shows the phase difference between the input signal and the signal from the balance as a function of \( \lambda_0 \). All experiments show straight lines. The loss angle can be determined from these figures by extrapolation to \( \lambda_0=0 \), to correct for the traveling distance of the wave.

Figure 5.7 and figure 5.8 summarize the calculated absolute values and the loss angle of the Gibbs modulus.

Unfortunately is it impossible to give a good interpretation of the data because of some instrumental problems. The generating barriers had a large mechanical hysteresis. The wave generated in the surface was not an exact sinus wave. Figure 5.9 shows schematically the shape of the displacement as a function of the input signal.

A second problem that occurred was probably the large amount of leakage of surfactant around the barriers. Hence the motion of the barriers was only effective for the surface deformation to a small extend. The leakage is probably dependent on the frequency of the wave too, which is a further complication of the leakage problem. The resulting surface tension gradients are not representable to determine the Gibbs elasticity with enough accuracy.

However the results are good enough to proceed with the investigations in future. Some modifications to the barriers and the driving mechanisms of the barriers are necessary.
Figure 5.5 Amplitude of the interfacial tension as a function of the reciprocal distance between the barrier and the Wilhelmy plate.

△ 0.2 Hz; ● 0.4 Hz; ▼ 0.7 Hz; ◆ 1.0 Hz; ■ 1.3 Hz and ▼ 1.6 Hz.

Figure 5.6 Phase difference between the input signal and the measured interfacial tension fluctuations as a function of the distance between the barrier and the Wilhelmy plate. Symbols see figure 5.5.
Figure 5.7 Absolute value of the Gibbs modulus as a function of the frequency. [SDS] = 0.001 mol/l.

Figure 5.8 Loss angle as a function of the frequency. [SDS] = 0.001 mol/l
Figure 5.9 Hysteresis in between the driving signal of the barriers and their displacement.

5.5 References

Chapter 6

Conclusions

In this thesis an attempt was made to elucidate the mechanisms of the transport of emulsions through porous media. This was done by measuring permeability changes of the porous cores caused by the emulsions and the transient droplet size distributions of the effluent emulsions. A microscopic pore model was developed, describing the interaction of an emulsion droplet and a funnel-like pore narrowing. The emulsions used in this study were dilute n-decane+carbon tetrachloride in water emulsions, stabilized with either Aerosol OT (AOT) or sodium oleate (NaOl).

Prior to the investigation of this main subject, the stability of the emulsions used was studied as a function of the sodium chloride concentration. It was found that the AOT stabilized emulsions were less stable at low electrolyte concentrations than the NaOl stabilized emulsions, and showed a much less pronounced critical coagulation concentration. This difference in behaviour is not expected on the basis of ζ-potentials: AOT stabilized emulsions were characterized at low electrolyte concentrations, by slightly larger absolute values of the ζ-potential. Calculation of the energy of interaction between the emulsion droplets for undeformed spherical droplets and for deformed droplets, having flat contact area, showed that electrostatic stabilization can occur neither for AOT stabilized emulsions nor for NaOl stabilized emulsions if two approaching droplets always deform. The data consistent with the hypothesis that the droplets of the AOT stabilized emulsion are easier deformable, resulting in a less steep decrease in coagulation rate constant with decreasing NaCl concentration.
However this process of deformation is a kinetic effect: not all droplet pairs show this deformation. Some electrostatic stabilization is present even in AOT stabilized emulsions, since NaCl addition does destabilize them, although the transition is more gradual than found for NaOl stabilized emulsions.

The experiments with the porous cores showed that the droplet size distribution had a large influence on the permeability reduction. It was found that broad size distributions of the emulsions lead to an inhomogeneous saturation of the porous medium. Most of the emulsion droplets are captured in the porous medium near the injection plane of the core.

The difference in stability between the two kinds of emulsion used, were confirmed with the flow experiments: the AOT stabilized emulsions coalesced in the porous medium. These results, together with the results of the emulsion stability measurements lead to the conclusion that the interfacial rheological parameters of the emulsion system have an important contribution in the behaviour of the emulsion. An attempt was made to measure these interfacial rheological data, but due to instrumental problems no real measurements could be performed.

Measurements of the transient droplet size distributions showed a significant contribution of the electrostatic interaction between the pore wall and the droplets to the plugging mechanism of the pore. Reducing this electrostatic repulsion leads to a faster decrease of the permeability, because the droplets can enter the pores faster. The final permeability of the medium is however higher, since the total resulting force acting on the droplets in the direction of the flow is higher, so that more droplets will be squeezed through the pore throats.

With the microscopic pore model the magnitude of these forces was calculated. From these results it could be concluded that the hydrodynamic drag for particles smaller than the pore throat was much larger than the colloidal interactions, so that the particles will always pass these pores. For the particles larger than the pore throat the hydrodynamic force is also larger than the colloid chemical interactions, but the hydrodynamic force could only be calculated for a particle position not too close to the pore wall. Deformation of the particle will probably occur, resulting in an increase of the electrostatic repulsion and capillary forces.
Chapter 7

Summary

In this thesis a study of the flow of emulsions through porous media is presented. The flow of emulsions in general and through porous media, is a very important aspect for the production of crude oil. Most crude oils are found and explored as emulsions. Often oil industry produces waste water containing some oil, which may be disposed by injection in empty reservoir rocks. This injection can cause a very high permeability reduction of these rocks, which makes further injection impossible.

In chapter 1 an introduction about emulsions, their stability and their use in practice is described. Special attention was payed to the production of oil and to the occurring flow of emulsions through porous media in this industry.

In the investigation described in this thesis, a model system was used to elucidate the mechanism of the permeability reduction by the flow of emulsions through porous cores. The emulsions used were dilute n-decane+carbon tetrachloride in water emulsions, stabilized with sodium oleate or Aerosol OT. The porous cores used were packed beds of glass beads.

Chapter 2 contains a description of the investigation of the stability of the emulsions used in this study. This was done by measuring the particle concentration as function of time and electrolyte concentration using a Coulter Counter. From these data a coagulation rate constant for the demulsification process was determined. The NaO1 stabilized emulsions were more stable at low electrolyte concentration than the AOT stabilized
emulsions and showed a much more pronounced transition from stable to unstable at the critical coagulation concentration (i.e. the concentration above which the coagulation rate constant becomes independent of the electrolyte concentration). However the $\zeta$-potentials of both emulsions predicted about the same stability. A hypothesis to explain this difference in behaviour of the emulsions was suggested using the calculated interaction energies for undeformed droplets and droplets deformed so that they had a flat contact surface. The droplets of AOT stabilized emulsion are probably easier deformable, resulting in the observed behaviour.

Chapter 3 describes the results of the transport of the emulsions through porous media. It was found that the polydispersity of the emulsions (droplet diameters between 1 and 10 $\mu$m) caused an inhomogeneous saturation with oil of the porous core. Most of the oil droplets were captured near the injection plane of the porous medium. The saturation is also a function of the flow rate of the emulsion, resulting in a larger permeability reduction for lower flow rates.

The NaO1 stabilized emulsions showed a strong electrostatic repulsion between the droplets and between the droplets and the pore wall. This was concluded from the transient droplet size distributions of the effluent emulsion.

Using the AOT stabilized emulsions, coalescence of the drops occurred during the flow through the porous core. This confirms the results of the stability measurements described in chapter 2.

A microscopic pore model describing the interaction between a spherical particle and a funnel-like pore is presented in chapter 4. The model calculates the London-Van Der Waals attraction and the electrostatic repulsion between the droplet and the pore wall. Also the hydrodynamic drag force acting on the droplet due to the flow of the continuous phase is calculated. The results showed that for particles smaller than the pore throat, the colloidal interactions could be neglected. For particles larger than the pore throat, the hydrodynamic force is also large. However, the hydrodynamic force on the particle near could only be calculated for particle positions up to a certain distance from the pore wall. of the lowest position of the particle in the pore. It is expected that in this position deformation
of the particle can occur, resulting in an increase of the electrostatic repulsion and appearance of capillary forces.

From the results of the previous chapter it was concluded that the deformability of the emulsion droplets plays an important role in the stability of the emulsions and the plugging mechanism in the pores. In chapter 5 a preliminary attempt to measure the interfacial rheological parameters describing this deformability is presented. Due to instrumental problems, it was not yet possible to measure the interfacial rheology of the emulsion systems described in this thesis. In spite of these problems, the method used is promising good results in future.

In appendix I an alternative method for measuring the interfacial tension is discussed. The force acting on a sphere passing a liquid-liquid or liquid-gas interface is used to determine the interfacial tension and the contact angle of the three phase contact line. The method is useful for prediction of capillary forces in porous media: if a sphere made of the porous material is used, one can directly measure the interfacial tension and the contact angle for the situation in the pores.

Finally, chapter 6 gives some concluding remarks on the investigations presented in this thesis.
Chapter 8

Samenvatting

Dit proefschrift beschrijft een onderzoek van het transport van emulsies door poreuze media. De stoming van emulsies in het algemeen en door poreuze media in het bijzonder, is een belangrijk aspect bij de productie van ruwe olie. Bijna alle ruwe olie wordt gevonden en gewonnen in de vorm van emulsies. Vaak wordt bij de produktie van olie afvalwater geproduceerd, dat nog een geringe hoeveelheid olie bevat. Dit afvalwater kan in lege olieformaties worden teruggepompt, waardoor vaak een sterke reduktie van de permeabiliteit van het gesteente optreedt. Hierdoor wordt het dan verder onmogelijk meer olie in de formaties te injecteren.

Hoofdstuk 1 beschrijft een algemene inleiding over emulsies, waarbij speciale aandacht aan de winning van olie en het daarbij optredende transport van emulsies door poreuze media wordt geschonken.

Voor het onderzoek beschreven in dit proefschrift werd een modelsysteem gebruikt om het mechanisme achter de permeabiliteitsreductie op te helderen. De emulsies die hiervoor gebruikt werden, waren n-dekaan+tetrachloormethaan emulsies gestabiliseerd met natrium oleaat of Aerosol OT. De poreuze media bestonden uit gepakte bedden van glasbolletjes.

In hoofdstuk 2 wordt het onderzoek naar de stabiliteit van de gebruikte emulsies beschreven. Dit onderzoek werd uitgevoerd door deeltjes concentraties als functie van tijd en zout concentratie te meten met een Coulter Counter. Met deze gegevens werd dan de coagulatiesnelheidsconstante van het demulsificatie process van de emulsie bepaald. Het
bleek dat de emulsies die gestabiliseerd waren met NaOl bij lage electrolyt-concentraties, stabieker waren dan de met AOT gestabiliseerde emulsies. Bovendien werd voor de NaOl emulsies een veel duidelijker overgang van stabiel naar onstabiel bij de kritische coagulatie concentratie (de zoutconcentratie waarboven de coagulatiesnelheidsconstante onafhankelijk van de zout concentratie wordt). Uit het ζ-potentiaalverloop werd echter ongeveer dezelfde stabiliteit voor beide typen emulsies voorspeld. Er wordt een hypothese gesuggereerd die het verschil in gedrag tussen beide emulsies verklaart, gebaseerd op de berekende interactie energieën van niet gede-formeerde bolvormige deeltjes en afgeplatte deeltjes. Het blijkt uit deze berekeningen, dat zowel de NaOl- als de AOT-gestabiliseerde emulsies electrostatisch niet zouden kunnen worden gestabiliseerd, als twee elkaar naderende deeltjes steeds zouden worden gedeformeerd. Het bestaan van een electrostatische repulsie volgt uit de invloed van NaCl; het verschil tussen de twee soorten emulsies moet dus eerer aan kinetische dan aan energetische factoren worden toegeschreven: druppels in AOT-gestabiliseerde emulsies worden gemakkelijker gedeformeerd.

Hoofdstuk 3 beschrijft de resultaten van het transport van emulsies door poreuze media. De polydispersiteit van de emulsies (deeltjesgrootte tussen 1 en 10 µm) bleek een niet homogene verzadiging van de poreuze media te veroorzaken. Het merendeel van de emulsiedruppels werd al vlak achter het injectievak afgevangen. De verzadiging van het poreuze medium bleek ook afhankelijk te zijn van de stroomsnelheid van de emulsie: een kleinere permeabiliteitsreductie bleek op te treden bij hogere stroom-snelheden.

De natriumoleaat gestabiliseerde emulsies vertoonden een sterke electrostatische repulsie tussen de druppels onderling en tussen de druppel en de poriewanden. Dit kon geconcludeerd worden uit de transiente poriegrootteverdelingen van de effluent emulsies.

De AOT gestabiliseerde emulsies bleken in het poreuze medium te coalesceren. Dit bevestigt de resultaten uit hoofdstuk 2.

Een microscopisch poriemodel dat de interactie tussen een bolvormig deeltje en een trechtermvormige porie beschrijft, wordt besproken in hoofdstuk 4. Het model berekent de London-van der Waals attractie en de electrostatische repulsie tussen het druppeltje en de poriewand. Ook wordt
de hydrodynamische meesleepkracht, die op het deeltje werkt, berekend. Uit de resultaten kan geconcludeerd worden, dat voor deeltjes kleiner dan de uitstroomopening van de porie, de colloidchemische interacties kunnen worden verwaarloosd. Voor grotere deeltjes is de hydrodynamische kracht ook erg groot. De hydrodynamische kracht kon echter slechts worden berekend voor deeltjes, die nog iets verwijderd zijn van de laagste positie in de porie. Verwacht wordt, dat in die situatie deformatie van het druppeltje kan optreden, waardoor de electrostatische repulsie zal toenemen, en capillaire krachten zullen gaan optreden.

Uit de resultaten van de vorige hoofdstukken werd geconcludeerd, dat deformatie van de oliedruppels een belangrijke rol speelt bij de stabiliteit van de emulsies en het verstoppingsmechanisme van de poriën. Hoofdstuk 5 beschrijft een eerste aanzet tot het meten van de grensvlak reologische grootheden, die deze deformeerbaarheid beschrijven. Helaas konden ten gevolge van problemen van instrumentele aard nog geen metingen aan de in dit proefschrift gebruikte emulsies uitgevoerd worden. Ondanks deze problemen, is de methode toch veelbelovend voor de toekomst.

In appendix I wordt een alternatieve methode voor de meting van grensvlakspanningen besproken. Hierbij wordt de kracht op een bolletje gemeten bij passage door een vloeistof-vloeistof of vloeistof-gas grensvlak. Uit deze kracht kan dan de contacthoek van de drie fasen contactlijn en de grensvlakspanning worden bepaald. De methode kan zeer goed worden toegepast om capillaire effecten in het poreuze medium te voorspellen: indien een kogeltje van het poreuze materiaal gebruikt wordt kan via deze meting directe grensvlakspanning en contacthoek voor de situatie in de porie worden bepaald.

Als laatste worden in hoofdstuk 6 nog enkele conclusies getrokken uit de resultaten van dit onderzoek.
Appendix I

Sphere tensiometry

1.1 Introduction

To investigate the capillary forces in the porous medium, it is necessary to know the three-phase contact angle and the interfacial tension between the oil and the water phase. In the past many techniques have been developed to measure these quantities.

The measurement of the contact angle is in most cases performed by optical methods. The results can be very inaccurate, especially if the contact angle is small.

The techniques to determine the interfacial tension, give ambiguous results too. Different methods yield different values for the same system and many techniques have only poor reproducibility.

The methods based on force measurements applied to test specimens immersed into the interface are most generally applied. The most important test specimens are the Wilhelmy plate and the Du Nouy ring, both requiring complete wetting or a contact angle of 0°.

A less common test specimen is a sphere. The advantage of this method is that in one measurement one obtains the interfacial tension and the three phase contact angle. The value of the contact angle is not very accurate since it is difficult to create a test specimen with a sufficient smooth surface, but it permits a correction for the interfacial tension if wetting of the sphere is incomplete (θ<0°).
1.2 Theory

To calculate the interfacial tension using the sphere method, the force-path function of a particle moving through the interface between two fluid phases has to be known [1,2,3]. Figure I.1A shows the coordinates used in the calculation of the force-path function. The parameters describing the three phase contact line are denoted by a subscript "0".

To eliminate the density of the particle the sphere was balanced in the upper phase. This results in three components that contribute to the total force acting on the particle.

The first force component is a direct consequence of the interfacial tension, acting at a contact angle $\theta$ on the three phase contact line. The perimeter of this contact line is defined as $2\pi r_0 = 2\pi R \cos \alpha$. Since the system is axisymmetric only the vertical component of this force important. This component can be calculated from the total force due to the interfacial tension, which acts at an angle $\alpha+\theta$ with the z-axis.

$$F_\gamma = 2\pi R \gamma \cos \alpha \cos (\alpha+\theta)$$  \hspace{1cm} (I.1)
Here $\gamma$ is the interfacial tension, $\theta$ the contact angle and $\alpha$ the centre angle (See figure I.1A).

The second component of the force acting on the sphere is the buoyancy force:

$$F_B = -\frac{1}{3}\pi R^3 \Delta \rho g (2 + 3 \sin \alpha - \sin^3 \alpha)$$  \hspace{1cm} (I.2)

The third component is a hydrostatic term due to the level difference $h_0$ of the three phase contact line and the flat interface:

$$F_H = \pi R^2 \Delta \rho gh_0 \cos^2 \alpha$$  \hspace{1cm} (I.3)

The second and third term can be understood if we consider the situation in figure I.1B. The total force acting on the particle is equal to weight of the volume of the liquid between the meniscus and the hypothetical plane if no meniscus would be present. The force caused by the interfacial tension is equal to the volume denoted by I in figure I.1B. The second and third term of the total force is equal to the weight of the cylinder with radius $r_0$ and height $h_0$ (equation I.3) minus the weight of the spherical cap immersed into it (equation I.2). If we define the depth of immersion $s$ as the position of the centre of sphere relative to the flat interface, then $h_0$ can be replaced by the following relation:

$$h_0 = R \sin \alpha - s$$  \hspace{1cm} (I.4)

By introducing the following parameters,

$$F^* = \frac{F}{\pi \Delta \rho g R^3}, C^2 = \frac{\gamma}{\Delta \rho g R^2} \text{and} \ z = \frac{s}{R}$$  \hspace{1cm} (I.5)

the force-path function, can be made dimensionless:

$$F^* = 2C^2 \cos \alpha \cos (\alpha + \theta) - \frac{1}{3}(2 + 3 \sin \alpha - \sin^3 \alpha) + \cos^2 \alpha (\sin \alpha - z)$$  \hspace{1cm} (I.6)

This equation shows that, apart from the system parameters $C$ and $\theta$, the total force only depends on $\alpha$ and $z$. These quantities are related through
Figure I.2 Force-path functions for different contact angles.

the Laplace equation, describing the shape of the interface between the fluid phases:

\[
\frac{1}{R_1} + \frac{1}{R_2} = \frac{\Delta p g h}{\gamma}
\]

(I.7)

Here \( R_1 \) and \( R_2 \) are the two principle radii of curvature of the interface between the two liquid phases. In the system discussed here these radii are defined by [4]:

\[
\frac{1}{R_1} = \pm \frac{d^2 y}{dx^2} \left[ \left( \frac{dy}{dx} \right)^2 + 1 \right]^{3/2}
\]

(I.8)

\[
\frac{1}{R_2} = \pm \frac{dy}{dx} \left[ \left( \frac{dy}{dx} \right)^2 + 1 \right]^{1/2}
\]

(I.9)
Unfortunately this equation cannot be solved analytically. Huh and Scriven [5] described a numerical solution method. They give a large table in which the profiles of the menisci can be found.

Figure 1.2 shows a series of force-path functions for different contact angles. The curves have a maximum and a minimum. The vertical position of the sphere and the values of the force at these extreme points can be used to determine the contact angle and the interfacial tension. These curves can be used to determine the contact angle according to the method of Yarnold [6]. If the sphere is such a position that the interface is completely flat, the following conditions hold:

\[ h_0 = 0, \sin \alpha - z = 0 \text{ and } \alpha + \theta = \frac{\pi}{2} \quad (I.10) \]

Hence the first and the last term in equation I.6 will vanish and the remaining term will be the buoyancy, expressed as

\[ F^* = -\frac{1}{3}(2 + 3z - z^3) \quad (I.11) \]

At the point where this equation intersects the experimental force-path curve condition 5.10 is satisfied and the contact angle can be calculated: \( \theta = \arccos z \).

Fieber and Sonntag [3] proposed a formalism to calculate the contact angle and the interfacial tension without having to solve the Laplace equation. According to them the second and third term of equation I.6 can be neglected for large values of \( C \), which will be the case if the interfacial tension force is larger then the weight of the sphere. Neglecting the last two terms results in the following simple expressions for the centre angle \( \alpha \) at the extreme points of the force-path function:

\[ \alpha = -\frac{\theta}{2} \text{ (maximum), } \alpha = \frac{\pi}{2} - \frac{\theta}{2} \text{ (minimum)} \quad (I.11) \]

Fieber and Sonntag observed a deviation of the centre angle calculated with equation 5.11 to the exact centre angle of less then 0.5 degree for \( \log C > \cos^2 \theta \). Using these results they give an empirical iteration scheme.
to calculate the contact angle, using the maximum and the minimum of the force.

To calculate the value of $C$, once the contact angle is known, Fieber and Sonntag derived two approximate formulas, one for large values of $C$ and one for small values of $C$. Using these formulas it is unnecessary to solve the Laplace equation. The only data necessary to measure are the extreme points of the force path function. The approximation always yields an error in $C$ less than 0.001, which results in an error of 0.01 in the interfacial tension, if the density difference and the radius of the sphere are exactly known.

1.3 Experimental

Experiments were performed at the Institute of Physical Chemistry of the Academy of Sciences of the GDR in Berlin. The surface tension of water (doubly distilled) and the interfacial tension of a water/n-decane interface were measured.

The force-path functions were determined with a microbalance and a moving plateau, home made at the Academy of Sciences. The ascending and descending speed of the plateau was 1.25 mm/s. Lowering this speed had no effect on the resulting force-path function.

Test specimens were two glass spheres with radii of 1.49 mm and 2.89 mm respectively. They were connected to the balance with a platinum wire with a diameter of 0.75 mm. Before the measurement was performed, the sample beaker and the glass sphere were thoroughly cleaned with hot chromic acid.

1.4 Results and discussion

In table I.1 the data of the extreme points are summarized. The calculated contact angles and the interfacial tensions, calculated from the extreme points are shown in this table too. For the calculation of the latter the assumption of large values of $C$ [3] is used, since all values, except for the measurement with the air/water system with the large sphere, the
value is larger than 1. For the first measurement this results in a larger error.

The values of the water/air surface tension are too high compared to the commonly accepted value of 72 mN/m at 25°C [7]. The value of the decane/water interfacial tension is too low. Aveyard c.s. [8] measured a value of 52.30 mN/m at 20°C and gives an interfacial tension temperature gradient of -0.089 mN/m °C. At 25°C this gives a value of 51.87 mN/m.

The observed deviations can be due to a number of facts. First the used test specimens are not exactly spherical. This results in the effect that the meniscus around the sphere is not symmetrical. This can have a significant effect on the force path function.

The second problem, especially at the minimum in the force-path function is that the meniscus will be deformed by the wire connecting the sphere to the balance. If this wire is thick the meniscus will “jump” over to the wire before the real minimum is reached. This results in a total immersion of the sphere in the lower phase. The minimum values found will be too large (less negative).

The third problem that can occur is that the surface of the sphere is not homogeneously wetted. The contact angle will then depend on the depth of immersion and can change along the wetted perimeter. This will again give erroneous results, due to a deformation of the meniscus.

Probably this last effect caused the deviations in the measured values. The measured contact angles are relatively large for well cleaned glass surfaces. This indicates that the surface of the spheres was not smooth enough to perform an accurate measurement.
The results are a useful indication that the method can successfully be applied to measure the data necessary to predict capillary effects in a porous medium. It is recommended to investigate the method thoroughly in future.

Acknowledgement

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1.5 References

Appendix II

List of most important symbols

Chapter 1.

\( N_C \) Capillary number.
\( \nu \) Fluid velocity (m s\(^{-1}\)).
\( \eta \) Viscosity (N m\(^{-2}\) s\(^{-1}\))
\( \gamma \) Interfacial tension (N m\(^{-1}\))

Chapter 2

Section 2.2.1

\( r_p \) Particle radius (m).
\( \eta_0, \eta \) Viscosity of the dispersed phase and continuous phase respectively (N m\(^{-2}\) s\(^{-1}\)).
\( \Delta \rho \) Density difference between the continuous phase and the dispersed phase. (kg m\(^{-3}\)).
\( g \) Gravity constant = 9.82 m s\(^{-2}\).

Section 2.1.2

\( \lambda \) London-Van Der Waals constant (J m\(^{-6}\)).
\( q \) Number of atoms per unit volume (m\(^{-3}\)).
\( V_1, V_2 \) Volume of the bodies for calculating the London-Van Der Waals attraction (m\(^3\)).
\( r \) Distance between the volume elements for calculating the London-Van Der Waals interaction (m\(^3\)).
\( \varepsilon_0 \) Dielectric constant of vacuum = 8.85*10\(^{-12}\) (C V\(^{-1}\) m\(^{-1}\)).
\( \varepsilon_r \) Relative dielectric constant.
\( \Psi_0 \) Surface potential (V).
\( \kappa \) Debye length (m\(^{-1}\)).
\( h \) Distance between the surfaces of the particles (m).
\( G_E \) Gibbs free energy of interaction due to electrostatic repulsion between two particles (J).

Section 2.1.3

\( b \) Thickness of a fluid film between two flat interfaces of two deformed droplets (m).
\( \delta \) Thickness of the surfactant layer between two liquid phases (m).
\( b_{cr} \) Critical film thickness, below which coalescence occurs (m).
\( A_{ham} \) Hamaker constant (J).

Section 2.2

\( n \) Number of particles or droplets per unit volume (cts m\(^{-3}\)).
\( n_0 \) Initial particle or droplet concentration (cts m\(^{-3}\)).
\( n_1 \) Total number of primary particle not yet “reacted” per unit volume (cts m\(^{-3}\)).
\( n_v \) Total number of aggregates per unit volume (cts m\(^{-3}\)).
\( a \) Coagulation rate constant (ml cts\(^{-1}\) s\(^{-1}\))
\( t \) Time (s).
\( D \) Diffusion coefficient of a particle in the continuous phase (m\(^2\) s\(^{-1}\)).
\( m \) Number of particles in an aggregate after coalescence occurred.
\( K \) Coalescence rate coefficient (s\(^{-1}\)).

Section 2.3.2

\( \zeta \) \( \zeta \)-potential (V).
\( \Psi_S \) Stern potential (V).

Section 2.3.3

\( r \) Distance between the centres of two droplets (m).
List of most important symbols

\( h_{II} \) Distance between the flat sections of two deformed particles (m).

\( a_1, a_2 \) Radii of two (non-deformed) interacting droplets (m).

\( b_1, b_2 \) Radii of the spherical part of two (deformed) interacting droplets (m).

\( \theta_1, \theta_2 \) Angle defining the flat sections of two (deformed) interacting droplets.

\( V_{int}^{II} \) Interaction energy due to deformation of two interacting droplets (J).

\( V_{sec.min.}^{fs} \) Interaction energy of two flat surfaces at the secondary minimum (J).

Chapter 3

Section 3.2

\( v_s \) Superficial velocity (m s\(^{-1}\)).

\( K \) Permeability of a porous medium (m\(^2\)).

\( \eta \) Viscosity of the continuous phase (N m\(^{-2}\) s\(^{-1}\)).

\( L \) Length of the porous core (m).

\( d \) Particle diameter of the glass beads of the porous core (m).

\( \varepsilon \) Porosity.

Section 3.3

\( s, S \) Oil saturation and water saturation of the porous medium.

Section 3.4

\( \alpha \) Flow redistribution parameter

\( \Lambda_{SI} \) Filter coefficient (m-1).

\( c_i \) Dispersed phase concentration (% v/v).

\( \tau \) Number of injected pore volumes emulsion.

\( T \) Dimensionless shifted time variable.

\( Q \) Flow rate (m\(^3\) s\(^{-1}\)).

\( V_p \) Total pore volume of the porous core (m\(^3\)).
*Section 3.6.4*

- $K_{sp}$: Specific conductivity ($\Omega^{-1} \text{ m}^{-1} \text{ mol}^{-1}$).
- $E_s$: Streaming potential (V).

*Chapter 4*

*Section 4.2*

- $E_p$: Energy of attraction between one atom and a spherical particle (J).
- $a$: Distance between one atom and the centre of the spherical particle (m).
- $h$: Height of the particle in the pore (m).
- $R_p$: Particle radius (m).
- $R_1$: Upper pore diameter (m).
- $R_2$: Lower pore diameter (m).
- $E_1, E_2, E_3$: Terms of the total energy of attraction (J).
- $E_A$: Total energy of attraction (J).
- $F_A$: Attractive force between the particle and the pore (N).

*Section 4.3*

- $\Psi$: Surface potential (V).
- $z_{\pm}$: Valency of the ions.
- $e_0$: Charge of an electron.
- $n_0$: Number of ions per unit volume ($\text{m}^{-3}$).
- $k$: Boltzmann constant = $1.38 \times 10^{-23}$ (J K$^{-1}$).
- $T$: Absolute temperature (K).
- $\kappa$: Reciprocal double layer thickness or reciprocal Debije length (m$^{-1}$).
- $\psi$: Dimensionless potential.
- $p$: Osmotic pressure (N m$^{-2}$).
- $F_R$: Repulsive force (n).

*Section 4.4*

- $u$: Fluid velocity vector (m s$^{-1}$).
- $p$: Pressure (N m$^{-1}$).
List of most important symbols

\[ U_0 \] Characteristic velocity equal to the maximum fluid velocity of the inlet profile (m s\(^{-1}\)).

\[ Re \] Reynolds’ number.

\[ \tau \] Penalty function parameter.

\[ C_D \] Drag coefficient.

\[ \xi \] Vorticity \( \nabla \times \mathbf{u} \)

Chapter 5

Section 5.1

\[ \varepsilon \] Gibbs elasticity (N m\(^{-1}\)).

\[ \gamma \] Interfacial tension (N m\(^{-1}\)).

\[ A \] Surface area of the interface (m\(^2\)).

\[ \theta \] Loss angle.

\[ \omega \] Angular velocity (rad s\(^{-1}\)).

\[ \xi_B \] Barrier amplitude (m).

\[ \kappa \] Wave number (m\(^{-1}\)).

\[ \beta \] Damping coefficient (m\(^{-1}\)).

\[ k \] Complex wave number \( = \kappa - i\beta \) (m\(^{-1}\)).

\[ W \] Dimensionless damping factor.

\[ B \] Dimensionless loss angle

\[ D \] Dimensionless distance.
Dankwoord

Hierbij wil ik al diegenen bedanken zonder wie bijdrage dit proefschrift niet tot stand kon komen.


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Curriculum Vitae


Hij is op 17 mei 1990 getrouwd met Roberta Caris. Sinds 1 oktober 1990 werkt hij als projectleider bestrijdingsmiddelen bij het Keuringsinstituut voor Waterleidingartikelen N.V. (KIWA) te Nieuwegein.
Stellingen
behorende bij het proefschrift van
J.A.M.H. Hofman

1. Modellen voor stroming van emulsies door poreuze media zoals voorgesteld door Alvarado en Marsden, waarbij de emulsies worden gezien als een "power-law" vloeistof, dragen niet bij tot de opheldering van het verstoppingismechanisme van poreuze media.

Dit proefschrift, hoofdstuk 3.

2. De in het verleden uitgevoerde onderzoeksprojecten op het gebied van stroming van emulsies door poreuze media houden in onvoldoende mate rekening met de interactie tussen de druppels en het poriemateriaal, en met de deformeerbaarheid van de druppels.

Dit proefschrift, hoofdstuk 2, 3 en 4.

3. Om de verwijdering van bestrijdingsmiddelen uit (drink)water met behulp van omgekeerde osmose te bestuderen, is het noodzakelijk om het adsorberend vermogen van het membraan ten aanzien van de bestrijdingsmiddelen te meten.

4. De conclusie, dat de aanwezigheid van grafietdeeltjes tijdens een emulsiopolymerisatie in afwezigheid van zeep tot hogere moleculargewichten van het polymer leidt, kan niet getrokken worden op grond van een vergelijking met een systeem verkregen door een solutiepolymerisatie.

T.G. Yamaguchi, T. Omo, Y. Saito, Chem. Ind., 5 okt. 1979, 784-785

5. De door Han et al. gevonden "onverklaarbare" resultaten bij experimenten met titanaten gemodificeerde vulstoffen in polymere matrizes, zijn gemak-
kelijk te verklaren wanneer men rekening houdt met de werkelijke samenstelling van commerciële titanaten.


6. De lagere “graft efficiency” gevonden voor polymerisaties, geïnitieerd door AZDP, kunnen wellicht mede veroorzaakt zijn door sterische hindering of een “kooi”-effect op het oppervlak van CaCO₃.


7. Het feit dat een bepaald oplosmiddel sneller fotochemisch wordt geoxideerd dan conventionele oplosmiddelen of slechts zeer traag biodegradeerbaar is in water, is nog geen garantie voor zijn milieuvriendelijkheid.


8. Het beleid van de Nederlandse Spoorwegen spoort niet met het beleid van de overheid om forenzen te stimuleren meer gebruik te maken van het openbaar vervoer.

9. Het stellen van maxima aan het aantal bekeuringen, dat mag worden uitgeschreven voor verkeersovertredingen, komt de verkeersveiligheid niet ten goede.

10. Vergelijking 3.7 in het proefschrift van Kuin is onjuist.


11. Het verdient aanbeveling typefouten, tenminste op de kaft van een proefschrift, zoveel mogelijk te vermijden: “Electrokinetic and hydrodynamic transport trough porous media”.

A.J. Kuin, Proefschrift TUE (1986)