TWO-PHASE REACTIVE TRANSPORT
OF AN OIL-SOLUBLE CHEMICAL

an NMR study
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Chapter 1

Introduction

The subject of the thesis is reactive transport of an Oil-Soluble Chemical (OSC) in two-phase systems. It was inspired by the need for new high-performance chemicals to reduce water production in oil and gas production wells. The context or background is discussed first, followed by a short description of the concept of OSCs for water control. Related studies are briefly reviewed. Finally, the scope and outline of the thesis are discussed.

1.1 Water control using gels

Each year many billions of barrels of water are produced world-wide, especially in the maturing oil fields. The produced water can stem from natural waterdrive or waterflood through the mechanisms of coning, casing leaks or channeling [1]. The produced water compromises the oil recovery and is expensive to dispose of. It was estimated that the cost-savings for the oil industry amount to about 100 million USD per year for each 1% reduction in produced water [1].

Water control or water shut-off can be accomplished by several methods. The traditional method is to squeeze a cement in the near-wellbore formation which hardens once in place [2]. However, some problems are associated with cement squeeze [3]. First, the slurry is very viscous, so that a very low injection rate needs to be applied in order to remain under the critical fracturing pressure. Secondly, due to the brittle nature of cements the blocking capacity may be temporary. Furthermore, since the cement slurry is a dispersion of solids the risk exists that the permeability of the oil-producing zones is damaged.

In Enhanced Oil Recovery (EOR) [4] the water control procedure often involves the injection of gel-forming chemicals (also referred to as gelants) into the near-wellbore formation. Ideally, the formed gel changes the permeability of the reservoir rock selectively such that the oil flow is not hindered, whereas the water flow is reduced or blocked completely. The principle of this process in illustrated in Figure 1.1.

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Many gel systems have been tested and applied in the field. Often the results are unpublished, classified or reported in little detail. Nevertheless, 30–40% of the treatments proved to be successful over many years [3], whereas others were successful only temporarily or failed completely [5–7]. Depending on reservoir conditions and economical restrictions each problem faced requires a specific choice of gelant and treatment procedure. Most gel systems have been investigated in the laboratory on chemical behavior and performance. The majority of the applied and tested gelants are aqueous based,
1. Introduction

Fig. 1.1: Principle of gel treatment in a reservoir after water breakthrough. The reservoir consists of a low-permeable oil-producing layer and a high-permeable watered-out layer (1). The gelant is injected through the production well and penetrates both layers (2). The gel is formed during shut-in after which the production is resumed. A traditional aqueous gelant forms a gel in both layers (3a). An Oil-Soluble Chemical selectively forms a gel (3b).

\textit{i.e.} the chemicals are injected in the reservoir as an aqueous solution and form a gel in the aqueous phase. Examples of these chemicals are: polyacrylamide [8, 9], vinylpyrrolidone/acylate copolymers [10], Xanthan [11], and silicate esters [12]. Alternatively, most chemicals require an organic or inorganic cross-linker. Aqueous gels that form a strong blocking gel are adequate only when the water producing layer can be isolated from the oil producing layer in the reservoir, so that the gel is formed only in the water producing layer. Alternatively, some weak gels are known to exhibit a so-called \textit{Disproportionate Permeability Reduction} (DPR) when placed inside porous materials [5, 6, 13–15], which means that they reduce the relative permeability to water more than that to oil. There is still a wide discussion about the exact mechanisms that bring about a DPR effect [16–22]. Furthermore, such types of gels, when placed in the near-wellbore area by bullheading\(^1\), may hamper the overall production altogether due to accumulation of water and the subsequent loss of oil phase mobility [23].

\(^1\) The term \textit{"bullheading"} means that the fluids of interest are pumped directly into the formation, usually through the wellbore, without mechanical isolation of specific layers.
1.2 Oil-Soluble Chemicals

A novel concept in water shut-off is the application of an Oil-Soluble Chemical (OSC) which is soluble and chemically stable in oil but reacts with water to form a gel. By using an OSC the gelant will selectively form a gel in the reservoir without blocking the oil producing layers.

The chemical tetra-methyl-ortho-silicate (TMOS) is a potential OSC for water shut-off. Like other alkoxy-silanes TMOS undergoes a heterogeneous gel reaction when mixed with water according to the sol-gel principle [24]. When an oleic solution of TMOS is injected in a porous medium (e.g. a reservoir) which contains water, the TMOS transfers to the aqueous phase where it undergoes the gel reaction. Consider a reservoir that consists of a low-permeable oil-producing layer and a high-permeable watered-out layer (see Figure 1.2). A solution of TMOS in oil is forced, for instance through an existing production well, into both layers. As a result the mixture penetrates into the reservoir and displaces the original fluids. In the oil-producing layer the TMOS remains stable and will not react. However, in the water-producing layer the TMOS will react on a pore scale with the water near the displacement front and with the residual water behind the front. Subsequently, a shut-in of the near-wellbore area is performed to allow the gel to cure. Ideally, upon resumption of the production the gel effectively blocks the water-producing layer while the oil-producing layer is not affected by the gel treatment (see Figure 1.1).

![Fig. 1.2: A bi-layered reservoir after water breakthrough (left). A mixture of TMOS and oil is injected in both layers. In the water-producing layer the TMOS is transferred from the oleic to the aqueous phase on the pore scale (right), where it undergoes a heterogeneous gel reaction.](image)

The application of alkoxy-silanes, in the context of water control, was first proposed by Plazanet and Thomere for the consolidation of sand producing formations during oil recovery [25]. Later, Thompson and Fogler considered the use of OSCs as diverting agents in both acid preflush and water control procedures. They performed laboratory experiments by injecting oleic solutions of either polyurethane or TMOS into micromodels and ceramic or limestone cores [20, 26]. Their study was focussed on pressure profiles, tracers and effluent analysis. Polyurethane was found not to be effective for the alteration of the (water phase) permeability [26]. Their micromodel visualization experiments showed the mass transfer of TMOS and the fluid/gel distribution on a pore scale, but the mechanisms remained unclear [27].
Two inter-European cooperation projects devoted considerable effort to evaluate the potential of TMOS as a bullhead water control agent [3]. The micromodel and core injection studies, conducted in these projects, were reported by Grattoni et al. [28, 29] and Bartosek et al. [30]. The effect of aging of TMOS-based gels was analyzed as well as the mechanisms of permeability modification. Recently, Elewaut et al. and Elewaut and Zitha reported experimental studies of TMOS gel treatments in sandstone cores, using pressure data [31] and X-Ray computed tomography (CT) imaging [32]. The mass transfer of the flowing gelant in the initial stages of the gel treatment was interpreted in a macroscopic sense. Other (potential) types of OSCs for water shut-off have not been reported so far, except for tetra-ethyl-ortho-silicate (TEOS) [30], which is related to TMOS. However, the reaction of TEOS with water is much slower than the reaction of TMOS with water [24].

1.3 Scope of thesis

The aim of the research was to investigate, on a fundamental level, the reactive transport of an oil-soluble gelant in two-phase systems, in bulk and within porous materials. A clear understanding of the physical-chemical mechanisms is lacking in literature. TMOS was chosen as a model chemical. The choice is inspired by the potential use of TMOS for water shut-off in hydrocarbon reservoirs. The effect of physical-chemical parameters, such as temperature, pH and concentration on the reactive transport was investigated, since the gel reaction is known to be sensitive to these parameters [24, 33–35]. The results described in the thesis form a framework for the reactive transport of oil-soluble gelants in general, as well as a framework for the experimental techniques needed in the analysis.

![Fig. 1.3: The role of relaxation times in NMR imaging. (left) High-resolution $T_1$-weighted NMR image of a glass bead pack saturated with oil in the upper part and water in the lower part. (right) $T_2$ map of a slice of a chocolate-peanut candybar.](image)

The main experimental tool used in this study is Nuclear Magnetic Resonance (NMR) [36]. Like other techniques (e.g. X-Ray CT imaging [37] or Scanning Neutron Radiography
1.4 Outline of thesis

NMR is a non-intrusive technique which can be employed to study (reactive) transport in porous media in situ. NMR imaging and spectroscopy are powerful tools and are widely used in (bio-)medicine [39] and chemistry [40]. A brief introduction to NMR is given in Appendix A. NMR techniques are based on radio frequency (rf) energy absorption by and emission from elements whose nuclei have a nonzero nuclear magnetic moment. In an NMR measurement the nuclei exhibit characteristic relaxation times ($T_1$ and $T_2$; see Appendix A) which depend on the chemical and physical conditions [41]. In many NMR imaging (MRI) applications the spatial variation in $T_1$ or $T_2$ within a sample is utilized to obtain spatial contrast based on $T_1$ or $T_2$ (see for example Figure 1.3). In our study we focus on the relaxation times $T_1$ and $T_2$ in order to monitor the reactive transport of TMOS in bulk and porous materials.

1.4 Outline of thesis

The first part (Chapters 2, 3, 4 and 5) deals with the coupled mass transfer and gel reaction of TMOS in two-phase bulk systems. In the second part (Chapters 6, 7 and 8) the placement of the chemical in porous materials is analyzed. We note that Chapters 2, 3, 4, 6 and 7 are based on published articles or articles which are to be published. Therefore, some repetition of content is present in these chapters.

In Chapter 2 the experimental technique to monitor the coupled mass transfer and gel reaction in bulk systems is described in detail. The method and results of NMR relaxation time measurements on bulk model systems are discussed. Further analysis of the experimental results, described in Chapter 2, is presented in Chapter 3. This includes a basic mass transfer model and an interfacial tension analysis of the bulk systems. Chapter 4 deals with the results of a second set of bulk phase experiments in which the effect of $p$H on the reactive transfer was determined. It also sets a framework for the NMR response of the fluids and gels which were used (including heavy water) in the experiments with the porous materials. In Chapter 5 the cross-linking of the silica in the sol-gel is considered and described by a phenomenological model. The experimental study on the reactive transport of TMOS in sandstone is presented in Chapter 6. The focus is on the coupled mass transfer and gel reaction which were monitored using the NMR techniques. In Chapter 7 the results obtained from a series of beam bending experiments are presented, which show the effect of gel treatment on the permeability of sandstone. A numerical model of TMOS placement in porous materials is presented in Chapter 8, together with the simulation results. Finally, the general conclusions and an outlook are given in Chapter 9.
Part I

Two-phase bulk systems
Chapter 2

Coupled mass transfer and sol-gel reaction in a two-phase bulk system*

NMR imaging and relaxation time measurements were employed to monitor the mass transfer of TMOS from the oleic to the aqueous phase in a two-phase bulk system. The longitudinal relaxation time ($T_1$) was calibrated and used to determine the concentration of TMOS in n-hexadecane during the transfer. In the aqueous phase a sharp decrease in the transverse relaxation time ($T_2$) is observed which is attributed to the gel reaction. The point at which a minimum (or plateau) in $T_2$ is found, indicates the gelation point.

2.1 Introduction

A method to form silica gels commonly applied is the reaction of alkoxy-silanes with water according to the sol-gel principle [24]. A recent development is the use of these gel-forming compounds in two-phase systems, where the alkoxy-silane is initially mixed with a hydrocarbon phase. The gelation process involves the transfer of the chemical out of the oleic phase into an aqueous phase. Coupled to the mass transfer a heterogeneous reaction takes place, resulting in gelation of the aqueous phase. An application of this process was first proposed by Plazanet and Thomere for the consolidation of sand producing formations during oil recovery [25]. The placement and gelation of the chemical in model porous systems was analyzed by Thompson and Fogler [20, 42]. In a previous work we presented a Nuclear Magnetic Resonance (NMR) study of the mass transfer and gel reaction of TMOS in two-phase bulk systems and glass bead packs [43].

The gelation process of tetra-methyl-ortho-silicate (TMOS) with water can be described as follows. Initially, the TMOS hardly mixes with water because of its poor solubility [24, 34], but when TMOS molecules come in contact with water the following hydrolysis reaction takes place

$$\text{Si(OCH}_3\text{)}_4 + 4\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4 + 4\text{CH}_3\text{OH}.$$  \hspace{1cm} (2.1)

The reaction products, silicic acid and methanol, are easily miscible with water and the presence of methanol results in an enhanced solubility of TMOS in water. The second step is the polymerization or condensation of silicic acid:

$$\equiv \text{Si - OH} + \text{HO - Si} \equiv \rightleftharpoons \equiv \text{Si - O - Si} \equiv + \text{H}_2\text{O}.$$  \hspace{1cm} (2.2)

* Adapted from Castelijns et al., J. Appl. Phys. 100, 024961 (2006)
The rate and extent of both reactions are mainly dependent on temperature, pH, and concentrations [24, 35, 44–46]. The gelation process results in a homogeneous gel consisting of a branched silica network together with (free) water and methanol molecules. The gel network can be regarded as a percolation of smaller silica clusters that cover a certain (bounded) domain.

The gel time of a sol-gel solution can be determined from NMR relaxation measurements (see Appendix A for a short introduction to NMR). Dokter et al. [47] studied the gel reaction in alkaline silica solutions which start to gel after adding acid. They observed a decay in the time-dependent $T_2$ and the occurrence of a minimum in $T_2$ near the gel point. $^2$H-NMR measurements of gelling solutions using deuterated TMOS, water and methanol were carried out by Wonorahardjo et al. [48]. The longitudinal relaxation time in the rotating frame $T_{1\rho}$ of the solvents showed a transition in decay rate before and after gelation.

This chapter presents the results of a series of experiments as a detailed extension of the previous work [43]. The mass transfer and gelation process were studied in an idealized setting, namely in small, two-phase bulk systems. TMOS is mixed with $n$-hexadecane and placed in a cylinder together with water, after which the reactive transfer occurs. The process is monitored by means of NMR imaging and relaxation time measurements. With this technique the liquids and their spatial distribution are visualized inside the cylinder during the experiment. The method of NMR imaging is non-intrusive, so that the process is not disturbed by the analysis. The NMR signal obtained in the experiments is sensitive to the presence of hydrogen nuclei in the liquids. Since the hydrogen densities for the liquids and gels considered are almost equal, the discrimination among the components and the contrast in the images cannot be derived from the hydrogen density. Spectroscopic NMR imaging [39] is a useful tool to quantify chemical species, based on chemical shift, but this tool was not used, except for a few test measurements. The reason for this is that the magnetic field homogeneity in the set-up was not sufficient to allow for discrimination among the different -CH species. Secondly, when studying the reactive transport in porous materials, the presence of pore-scale magnetic gradients [49] would cause an additional line broadening. Instead, we developed an approach which is based on the relaxation times $T_1$ and $T_2$ of the hydrogen nuclei. It is noted that in our methods the NMR signal and relaxation times result from the combined NMR response of all hydrogen nuclei, i.e. the chemical shift [39] was not resolved in the frequency domain.

It was found empirically [43] that the relaxation times depend on the composition and temperature of the fluids. The relaxation times are related to the molecular mobilities. Since the viscosity is related to the molecular mobilities, the relaxation times can be correlated to the viscosity [43], at least for the pure components. By measuring the relaxation times of the liquid phases the concentration of TMOS in $n$-hexadecane can be determined, and also the rate of gelation in water can be characterized. To this end, the relaxation times were measured for a series of calibration samples, i.e. $n$-hexadecane/TMOS mixtures and a set of prepared gel samples.

The experiments with the two-phase systems were done at various temperatures, and with different concentrations of TMOS in $n$-hexadecane. Typical mass transfer rates and gel times are derived for each experiment. The gel times acquired with the NMR
2.2 Principle of nuclear magnetic relaxation in liquids

Measurements are based on the aqueous phase $T_2$. During the gel reaction $T_2$ decreases and levels off after several hours. The results are in agreement with the gel times obtained from tilting test tube experiments. Our analysis discusses the hydrogen $T_2$ spectra of the aqueous phase in detail and particularly the role of methanol in the solution.

In the following section we discuss a model that describes the relaxation in pure liquids. It also adequately describes the temperature and concentration dependency of $T_1$ for the binary TMOS-oil mixtures. The model shows that multi-exponential relaxation behavior is expected in liquid mixtures. Furthermore, it will show that for different fluids, having different viscosities, differences in relaxation times are expected.

2.2 Principle of nuclear magnetic relaxation in liquids

This section summarizes briefly the main mechanisms of nuclear spin relaxation for hydrogen nuclei in pure liquids and simple binary mixtures.

2.2.1 Pure liquids

Consider a liquid which is placed and magnetized in an external magnetic field. If the longitudinal nuclear magnetization $M_z$ is reduced to zero, for instance by applying a 90° radio frequency (rf) pulse, it will relax back to its equilibrium magnitude $M_z(0)$ due to spin-lattice relaxation (see also Appendix A). The restoring magnetization is described by an exponential

$$M_z(t) = M_z(0) \left[ 1 - \exp \left( -\frac{t}{T_1} \right) \right] ,$$

where $T_1$ is the longitudinal relaxation time [36, 50]. The transverse magnetization $M_T$, which is equal to $M_T(0)$ just after the excitation of the system by the 90° pulse, decays back to zero due to spin-spin relaxation. This is described by the exponential

$$M_T(t) = M_T(0) \exp \left( -\frac{t}{T_2} \right) ,$$

where $T_2$ is the transverse relaxation time [36, 50].

The relaxation processes, both for $T_1$ and $T_2$, are due to intra- and inter-molecular interactions of the hydrogen nuclei and due to spin-rotational (SR) interactions [41, 51]. The overall relaxation times $T_1$ and $T_2$ are therefore given by

$$\frac{1}{T_1} = \left( \frac{1}{T_{1 \text{ intra}}} \right) + \left( \frac{1}{T_{1 \text{ inter}}} \right) + \left( \frac{1}{T_{1 \text{ SR}}} \right) ,$$

$$\frac{1}{T_2} = \left( \frac{1}{T_{2 \text{ intra}}} \right) + \left( \frac{1}{T_{2 \text{ inter}}} \right) + \left( \frac{1}{T_{2 \text{ SR}}} \right) .$$

Intra- and inter-molecular relaxation is driven by (fluctuating) dipole-dipole interactions between the hydrogen nuclei. In case of intra-molecular relaxation the interactions are modulated by the rotational motion of the molecule. The rotational correlation time (or
"tumbling" time) $\tau_c$ is of the order of 1–100 ps, which is often much shorter than the Larmor precession time of the nuclei, so that $\omega_0 \tau_c \ll 1$, where $\omega_0$ is the Larmor precession frequency. This situation is referred to as the fast motion limit [50]. In this limit $(T_1)^{-1}_{\text{intra}} = (T_2)^{-1}_{\text{intra}}$, and the intra-molecular relaxation rate for a many-nuclei molecule is given by [52]

$$\left(\frac{1}{T_{1,2}}\right)_{\text{intra}} = \frac{3}{2} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 h^2 \frac{2}{n_p} \left(\sum_{i>j} \frac{1}{r_{ij}^6}\right) \tau_c,$$  \hspace{1cm} (2.7)

where $\mu_0$, $\gamma$, $h$, and $n_p$ are the magnetic permeability, the gyromagnetic ratio, Planck’s constant, and the number of hydrogen nuclei per molecule, respectively. $r_{ij}$ are the distances between the nuclei $i$ and $j$. Eq. 2.7 shows that the relaxivity is proportional to a single correlation time, provided that the molecule is rigid, i.e. the distances $r_{ij}$ and the orientations of the nuclei remain constant. However, internal motion or anisotropic rotation leads to multiple correlation times [53].

An effective, Arrhenius type expression for the correlation time can be used assuming that the motions are thermally activated [54]:

$$\tau_{c,\text{eff}} = \tau' \exp\left(\frac{E_A}{RT}\right),$$  \hspace{1cm} (2.8)

where $\tau'$, $E_A$, $R$, and $T$ are the inverse frequency factor, the activation energy for rotational motion, the gas constant, and the temperature, respectively.

The inter-molecular contribution is linked to translational motion of the molecules. In the fast motion limit (where $(T_1)^{-1}_{\text{inter}} = (T_2)^{-1}_{\text{inter}}$), and with the approximation that all hydrogen nuclei are located at the center of the molecule, the relaxivity is expressed as [50, 55]

$$\left(\frac{1}{T_{1,2}}\right)_{\text{inter}} = \frac{\pi}{5} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 h^2 N_0 \frac{aD}{N_0},$$  \hspace{1cm} (2.9)

where $N_0$ is the number of hydrogen nuclei per unit volume, $D$ is the diffusivity of the molecules and $a$ is the closest radius of approach.

Finally, we neglect spin-rotational interactions, which are only important for some liquids containing small molecules, or gaseous systems [56]. The right-hand side of Eq. 2.5 therefore, reduces to the first two terms. From Eqs. 2.5, 2.7 and 2.9, the overall relaxivity for a single-component liquid is given by

$$\frac{1}{T_{1,2}} = \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 h^2 \left(\frac{3}{n_p} \sum_{i>j} \frac{1}{r_{ij}^6} \tau_{c,\text{eff}} + \frac{\pi}{5} \frac{N_0}{aD}\right).$$  \hspace{1cm} (2.10)

Although, in the fast motion limit the transverse relaxation time $T_2$ is equal to $T_1$, the experimentally observed relaxation time $T_2$ is sensitive to magnetic field inhomogeneities or gradients, and is often shorter than $T_1$.

### 2.2.2 Correlation of relaxation times with viscosity in pure liquids

The relaxation processes in the liquid are driven by the molecular motions. Since the viscosity $\eta$, which is a macroscopic bulk property, is related to the molecular motions,
the relaxation times can be correlated with \( \eta \). Instead of using the Arrhenius expression (Eq. 2.8) for the effective correlation time \( \tau_{c,\text{eff}} \), we can link the time to the rotational diffusion coefficient \( D_R \) of the molecules [50]. This diffusion coefficient follows from a Stokes-Einstein equation, so that [50, 51, 57]

\[
\tau_{c,\text{eff}} = \frac{1}{6D_R} \approx \frac{4\pi \eta a^3}{3k_BT},
\]

where \( k_B \) is the Boltzmann constant. Likewise, the diffusion coefficient \( D \) in Eq. 2.9 can be related to the viscosity \( \eta \) by

\[
D = \frac{k_BT}{C\alpha \eta},
\]

where \( C \) is a coefficient which is related to the molecular shape, amongst others [58]. Hence, it follows from Eq. 2.10 that

\[
\frac{1}{T_{1,2}} \propto \frac{\eta}{T}.
\]

Zega et al. [59] showed that, for a series of alkanes, the values of \( 1/T_1 \) against \( \eta/T \) can be plotted approximately on a single curve.

### 2.2.3 Binary mixtures

In a mixture of liquids \( A \) and \( B \), there is an additional inter-molecular contribution due to interaction between hydrogen nuclei of \( A \) and \( B \). The individual relaxation times \( T_{1,2}^A \) and \( T_{1,2}^B \) in the mixture are defined as an extension to Eq. 2.10 by

\[
\frac{1}{T_{1,2}^A} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^4 k^2 \left[ c_A \tau_{c,\text{eff},A} + \frac{\pi}{5a_A} \left( \frac{N_{0A}}{D_{AA}} + \frac{N_{0B}}{D_{AB}} \right) \right],
\]

\[
\frac{1}{T_{1,2}^B} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^4 k^2 \left[ c_B \tau_{c,\text{eff},B} + \frac{\pi}{5a_B} \left( \frac{N_{0A}}{D_{BA}} + \frac{N_{0B}}{D_{BB}} \right) \right],
\]

where \( c_A \) and \( c_B \) are constants related to the molecular structures, and \( D_{ij} \) are the mutual diffusion coefficients. Suppose the longitudinal magnetization of the mixture in equilibrium with an external magnetic field is brought to zero by a 90° rf pulse. Subsequently, based on superposition of the magnetic moments, the total magnetization shows a bi-exponential relaxation behavior as described by

\[
M_z(t) = M_z(0) \left[ 1 - f \exp \left( -\frac{t}{T_1^A} \right) - (1 - f) \exp \left( -\frac{t}{T_1^B} \right) \right],
\]

where \( f \) is the proton density fraction of \( A \). Thus, the proton fraction and the relaxation times are functions of composition. If \( T_1^A \) is equal or almost equal to \( T_1^B \) or in case \( f \) is close to zero or close to one \( M_z \) relaxes according to a single exponential as defined by Eq. 2.3. Similarly, the transverse magnetization of the mixture relaxes back to zero after application of the 90° pulse according to the bi-exponential function

\[
M_T(t) = M_T(0) \left[ f \exp \left( -\frac{t}{T_2^A} \right) + (1 - f) \exp \left( -\frac{t}{T_2^B} \right) \right].
\]

Eq. 2.16 and Eq. 2.17 can be extended to describe the multi-exponential relaxation in multi-component mixtures.
2.2.4 Correlation of relaxation times with viscosity in binary mixtures

In (simple) binary liquid mixtures the effective viscosity often depends on the composition, provided that the viscosities of the pure components, $\eta_A$ and $\eta_B$, are not equal to each other. Several mixture laws exist [60]. For example, the following mixture law was introduced by Grunberg and Nissan [61]:

$$\ln \eta_{\text{mix}} = x \ln \eta_A + (1 - x) \ln \eta_B + Gx(1 - x),$$

(2.18)

where $\eta_{\text{mix}}$ is the effective viscosity of the mixture, $x$ is the mole fraction of component $A$, and $G$ is an interaction parameter.

The relaxation times will be a function of composition (through the proton fractions belonging to the components A and B) as long as $T_{1A}^1$ is higher or lower than $T_{1B}^1$. If, in addition, $\eta_A$ is different from $\eta_B$, the relaxation times can be correlated with the effective viscosity via the composition dependence. On a molecular level, one can expect, in case $\eta_A \neq \eta_B$, the diffusivities of the molecules to be a function of the composition. The higher the viscosity, the lower are the diffusivities. This will affect the inter-molecular relaxation (see Eq. 2.9). As for intra-molecular relaxation, the effective correlation times of the species may depend on $\eta_{\text{mix}}$ as indicated by Eq. 2.11, but this is not always the case [62].

2.3 Experimental section

2.3.1 Chemicals and preparation

Tetra-methyl-ortho-silicate, Si(OCH$_3$)$_4$, was obtained from Aldrich (>99% pure). For the oleic phase, $n$-hexadecane, or $n$-C$_{16}$H$_{34}$ (obtained from Merck, >99% pure) was used as a clean and well-defined hydrocarbon liquid which has a significant difference in $T_1$ compared to water and TMOS. The viscosities of TMOS, $n$-hexadecane and mixtures of TMOS and $n$-hexadecane were measured at 25 °C with a rheometer (Contraves LS40). For the aqueous phase we used double-demineralized water.

Several gel samples were prepared at ambient conditions with demineralized water and TMOS in different volume ratios. The initial volume fraction $\phi_T$ (hence, also the mole fraction) of TMOS in the mixture was chosen to be a measure to characterize the final gel state. It was found that for 2.5 vol% (or 0.31 mol%) of TMOS in water no gel was formed, even after several months. For 5.0 vol% and more (tested up to 50 vol%) a homogeneous gel formed. It was observed that after several weeks the high-concentration gels showed a small degree of syneresis. Calibration solutions of methanol in demineralized water were prepared as well.

2.3.2 NMR apparatus and sequences

Relaxation times and $T_1$-weighted images of the samples were recorded with a 4.7 Tesla NMR spectrometer operating at a frequency of 200 MHz for $^1$H. The setup consists of a super-conducting magnet (Oxford Instruments, Oxon, UK) with a vertical, narrow-bore insert (Doty, Columbia, USA) with an inner diameter of 40 mm. The insert has
2.3. Experimental section

Fig. 2.1: Schematic representation of the 2D Turbo Spin Echo sequence. After the initial 90° rf pulse the 180° rf pulse and the subsequent read-out of the echo are repeated $N$ times, during which the phase encoding gradient is varied. In this example $N = 2$.

gradient coils capable of producing pulsed magnetic gradients up to 1 T/m in three directions. The insert is air-cooled, and the temperature inside is 22 ± 2 °C. However, for the experiments a poly-vinyl-chloride (PVC) sample holder was constructed in which a fluorocarbon fluid (Galden HT135, manufactured by Solvay Solexis) was circulated in order to control the temperature. The fluid is invisible to the NMR set-up and the temperature can be controlled between 10 and 65 °C with an accuracy of about 1 degree.

2D images were obtained with a Turbo Spin Echo (TSE) sequence [63]. A schematic view of the sequence is shown in Figure 2.1. A train of 180° rf pulses is used to produce a train of phase-encoded echoes, generating one spatial dimension. The second spatial dimension is obtained due to the presence of a frequency encoding gradient between the 90° pulse and the first 180° pulse. This gradient is also switched on during the acquisition of the echo signal, and is therefore referred to as read-out gradient. Self-diffusion coefficients were measured with the Pulsed Field Gradient (PFG) diffusion sequence [64], which is similar to the imaging sequence, however, two extra gradient pulses are applied before and after the 180° rf pulse to encode the signal, producing an attenuation that decreases with the self-diffusion coefficient.

The relaxation times in the samples were acquired using one-dimensional NMR methods. In absence of phase encoding gradients, these methods produce 1D profiles instead of 2D images. These profiles can be regarded as projections of the average signal in one direction. The longitudinal relaxation time $T_1$ was measured by a 1D Saturation Recovery sequence [65]. With this method the longitudinal magnetization $M_z$ of the sample is destroyed by applying a train of rf pulses of random length and with random intervals. Subsequently the magnetization restores to its equilibrium and its magnitude is probed by applying a single spin-echo sequence for multiple delay times. For the calibration of
the samples each $T_1$ curve was measured with a series of 25 spin echoes, logarithmically distributed over an interval of 16 s.

Transverse relaxation times were measured with a 1D Carr-Purcell-Meiboom-Gill (CPMG) method [36, 50], in which a spin-echo train is acquired by applying a $90^\circ - (\tau - 180^\circ - \tau)_n$ sequence of rf pulses, where $2\tau$ is the inter-echo time $\Delta \tau_E$. In this sequence the read-out gradients are applied as described above for the 2D TSE sequence. It is noted that the apparent relaxation time $T_{2,\text{apparent}}$ may contain a contribution due to diffusion similarly to the PFG method. For a single-component system the apparent $T_2$ can be expressed by (based on Ref. [64])

$$T_{2,\text{apparent}} = \left[ \frac{1}{T_2} + \frac{bD}{\Delta \tau_E} \right]^{-1},$$  

where $b$ is a diffusion weighting factor that depends on the timing, shape and strength of the gradients used. With respect to the read-out gradient the $b$-factor is approximately equal to $(\gamma G \delta/2)^2$, where $G$ is the gradient strength and $\delta$ is the duration of the read-out. The inter-echo time and the duration of the read-out were constantly taken as 7.2 ms and 0.5 ms, respectively. Each spin-echo train consists of a thousand echoes.

The CPMG spin-echo trains were analyzed with the inversion routine CONTIN [66] to give quasi-continuous $T_2$ spectra, consisting of a hundred points on a logarithmic $T_2$ axis. In case of mono-exponential relaxation the inversion produces one peak. Multi-exponential relaxation, which may occur in a mixture (see Section 2.2.3), results in more peaks. In general, the peaks in the spectrum, produced by the routine, broaden when the signal-to-noise ratio decreases, up to the point where the peaks cannot be distinguished from each other. The absolute minimum and maximum $T_2$ that can be resolved by the routine are determined by the echo time (7.2 ms) and the total length of the echo train (7.2 s), respectively. The produced spectra are sensitive especially to the signal of the leading echoes of the sequence, and proper $90^\circ$ and $180^\circ$ conditions of the rf pulses are therefore needed. An overview of the CPMG-data acquisition and data processing is given in Figure 2.2.

2.3.3 Bulk experiments

The two-phase bulk experiments were performed using cylindrical Teflon vials with an inner diameter of 18 mm. In each case 2.5 ml of water and 2.5 ml TMOS/n-hexadecane were placed in the vial. The fluids were preheated to the temperature of interest (25, 35 and 45 °C, respectively). The initial volume fraction of TMOS in n-hexadecane was 0.20 and 0.40, respectively, for each temperature considered. After injection, the samples were quickly placed in the NMR set-up. Subsequently, a continuous loop of NMR measuring sequences was executed: a $T_1$ measurement using the Saturation Recovery sequence, 2D imaging using the TSE sequence, and a $T_2$ measurement using the CPMG sequence. During each repetition the CPMG sequence was executed three times with a varying strength of the read-out gradient (50 mT/m, 100 mT/m and 200 mT/m).

For every sequence the read-out gradient was set in the vertical direction. The slice selection gradient was applied perpendicular to the read-out direction, yielding a vertical slice with a thickness of about 4 mm. The variation of the gradient strength in the
2.3. Experimental section

Fig. 2.2: Overview of the CPMG spin-echo train acquisition and data processing.

The experimental section describes the methodology used in the study, including the acquisition and processing of CPMG (Carr-Purcell-Meiboom-Gill) spin-echo train data. The CPMG spin-echo train is a sequence of RF pulses used to acquire relaxation data, which are then processed to yield time-dependent $T_2$ spectra.

The figure illustrates the CPMG spin echo train sequence, which consists of 90° and 180° pulses, followed by a delay time $t$. The spin echo intensity decays over time due to relaxation processes, and this decay is described by the function $exp(-t/T_2)$. The combined NMR response of all H-nuclei in liquids is shown, and the repetition of the sequence every 15 minutes yields time-dependent $T_2$ spectra.

A multi-exponential fit is applied to the data, and the results are presented in a table, showing the exponent, $T_2$ values, and amplitudes.

For the fast (dominant) component in the spectra, $T_2$ values are extracted using a Gaussian fit, and the resulting time-dependent $T_2$ spectra are shown.

The figure provides a visual representation of the experimental setup and data processing steps involved in the study.
Coupled mass transfer and sol-gel reaction in a two-phase bulk system

CPMG measurements and the constant read-out duration result in a varying resolution of the 1D profiles. Nevertheless, the liquid phases are easily reconstructed and identified from the profiles. The magnetic susceptibility of water and \( n \)-hexadecane is \(-9.0 \times 10^{-6}\), respectively, \(-8.0 \times 10^{-6}\) [67]. At 4.7 Tesla the resulting frequency mismatch is about 200 Hz. With respect to the applied read-out gradient of at least 2.6 kHz mm\(^{-1}\), susceptibility artifacts at the interface between \( n \)-hexadecane and water are insignificant. The acquisition time for each sequence is between 2 and 3 minutes, so that the loop time is about 15 minutes (given one Saturation Recovery, one 2D TSE and three CPMG measurements per loop).

In order to measure the gel time of the aqueous phase similar experiments were performed inside glass vials with equal dimensions as the Teflon vials. The vials were placed in a water bath at specific temperatures. By gently tilting the vials at times near the predicted gel time with intervals of 5 minutes, the gel time could be determined by checking whether the oil-water interface is still able to follow the tilting motion. The reproducibility was checked by using multiple glass vials, and the accuracy of the gel time is about 30 minutes.

2.4 Results and discussion

2.4.1 Calibration results

Viscosity measurements

The viscosities of TMOS, \( n \)-hexadecane and the mixtures were measured in order to check whether the relaxation times can be correlated with viscosity and temperature. Figure 2.3 shows \( \ln \eta_{\text{mix}} \) at 25 °C as a function of the mole fraction \( x \) (where \( x = 0 \) represents pure oil, and \( x = 1 \) represents pure TMOS). The viscosity for \( x = 0 \) is \( 3.01 \pm 0.01 \) mPa s, and it decreases monotonically with \( x \) to \( 0.63 \pm 0.01 \) mPa s when \( x = 1 \). The figure shows that \( \ln \eta_{\text{mix}} \) follows a straight line with increasing mole fraction. The values were fitted with the mixture law (Eq. 2.18) yielding an excellent fit with \( G = 0 \).

\( T_1 \) relaxation in TMOS/\( n \)-hexadecane mixtures

The calibrations are used to determine the concentration, \( \phi \), of TMOS in \( n \)-hexadecane in the two-phase bulk experiments. The Saturation Recovery data of the TMOS/\( n \)-hexadecane mixtures were evaluated by fitting mono-exponential and bi-exponential decay curves as given by Eqs. 2.3 and 2.16, respectively. For each concentration and temperature the decay appeared to be virtually mono-exponential and a robust bi-exponential fit could not be obtained. The individual \( T_1 \)-s for TMOS and \( n \)-hexadecane in the mixtures are obviously relatively close. Noise present in the spin-echo data results in significant errors in the fit parameters when applying a multi-exponential fit, even at high signal-to-noise ratios.

The Saturation Recovery data of the pure liquids were fitted straightforwardly with a single exponent. As for the mixtures, a slight deviation from mono-exponential behavior
2.4. Results and discussion

Fig. 2.3: Viscosity of the TMOS/n-hexadecane mixtures as a function of the mole fraction $x$ of TMOS. The solid curve represents the fit using the Grunberg-Nissan mixture law.

Fig. 2.4: Relaxation time $T_1$ of TMOS/n-hexadecane mixtures as a function of temperature. The concentration of TMOS for each curve is indicated by the symbols in the legend. A single-exponential $T_1$ was derived from the experimental data. The solid curves for the pure components indicate the fitted $T_1$. 
Coupled mass transfer and sol-gel reaction in a two-phase bulk system

was observed, especially for the intermediate concentrations. This causes the mono-
exponential fit to be sensitive to the distribution and length of the Saturation Recovery
intervals. The intervals are therefore fixed throughout the experiments. The accuracy
and reproducibility of the mono-exponential \( T_1 \) measurements was found to be within
5%. The results are shown in Figure 2.4. For \( n \)-hexadecane \( T_1 \) equals 0.763 s at 20.2 °C
and increases to 1.69 s at 66.7 °C. Figure 2.5 shows the reciprocal \( T_1 \) of \( n \)-hexadecane as
a function of \( \eta/T \) (the viscosity data were derived from literature [67]). The solid curve
in this figure is a linear fit through the data points, which shows that for \( n \)-hexadecane
Eq. 2.13 is satisfied. For pure TMOS \( T_1 \) equals 3.52 s at 21.2 °C and increases to 4.14
s at 66.3 °C. The viscosity of TMOS is not known for temperatures other than 25 °C.
Therefore, a plot of the reciprocal \( T_1 \) of TMOS against \( \eta/T \) is not presented.

In general, \( T_1 \) increases monotonically with concentration and with temperature (see
Figure 2.4). Using the viscosity data of the mixtures (measured at 25 °C) and the cal-
bibrations of \( T_1 \) we can plot the reciprocal \( T_1 \) of the mixtures against \( \eta_{\text{mix}}/T \). It can be
observed in Figure 2.6 that \( 1/T_1 \) increases monotonically with \( \eta_{\text{mix}}/T \), but not in a linear
manner.

Next, the experimental results are evaluated with the model equations for the re-
flexation. The inter-molecular contribution to the relaxation in Eqs. 2.14 and 2.15 is
calculated first. The numbers of protons \( N_{0A} \) and \( N_{0B} \) are derived from the concentra-
tion of TMOS in \( n \)-hexadecane. The radius of approach \( a \) is estimated based on the
molecular volume of the molecules. For \( n \)-hexadecane we take 5 Å, and for TMOS 4 Å.
The diffusion coefficients \( D_{ij} \) are not known precisely, and could not be determined. The
diffusion coefficient measured with the PFG method represents an average diffusivity of
the molecules. For all coefficients \( D_{ij} \) this average diffusion coefficient of the mixture is

Fig. 2.5: Reciprocal \( T_1 \) of \( n \)-hexadecane as a function of the viscosity-temperature ratio, \( \eta/T \).
The viscosity data is derived from literature [67]. The solid curve represents a linear
fit.
Fig. 2.6: Reciprocal $T_1$ (mono-exponential) of the TMOS/n-hexadecane mixtures as a function of the viscosity-temperature ratio, $\eta_{mix}/T$. $T$ is fixed at 25 °C.

Table 2.1: Fitting parameters for the relaxation time model of the pure liquids.

<table>
<thead>
<tr>
<th></th>
<th>n-hexadecane</th>
<th>TMOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau'$ [ps]</td>
<td>0.052</td>
<td>1.64</td>
</tr>
<tr>
<td>$E_A$ [kJ mol$^{-1}$]</td>
<td>15.2</td>
<td>2.46</td>
</tr>
<tr>
<td>$\tau_{c,\text{eff}}$ [ps] at 20 °C</td>
<td>26.7</td>
<td>4.49</td>
</tr>
</tbody>
</table>

used (not presented here), which seems acceptable given the value of the self-diffusion coefficient for the pure liquids (i.e. $1.59 \times 10^{-9}$ m$^2$ s$^{-1}$ for TMOS and $0.40 \times 10^{-9}$ m$^2$ s$^{-1}$ for n-hexadecane at 25 °C).

The intra-molecular part of the relaxation contains the effective correlation time $\tau_{c,\text{eff}}$ which is found by an optimization process as follows. For both species the correlation time $\tau_{c,\text{eff}}$ as defined in Eq. 2.8 is assumed to be independent of concentration, therefore the term is derived from the experimental data of pure TMOS and pure n-hexadecane, respectively. The predicted inter-molecular term is subtracted from the experimental, total $T_1$ for each temperature. Then the remainder is fitted as a function of temperature with Eqs. 2.7 and 2.8. The summation term $\sum r_{ij}^{-6}$ is estimated by considering a rigid molecular model for each species. The resulting fits for TMOS and n-hexadecane, yielding the unknown parameters $E_A$ and $\tau'$ (see Table 2.1), are shown in Figure 2.4 as the solid curves. The excellent fit indicates that the model equations adequately describe the spin-lattice relaxation of the pure liquids.

Finally, the total relaxation times in the mixture are calculated (defined by Eqs. 2.14 and 2.15) using the obtained fitting parameters (see Table 2.1). The Saturation Recovery decay is subsequently constructed as given by Eq. 2.16, and the result is fitted with
the mono-exponential decay function in order to compare the calculated values to the experimental results. The comparison is shown in Figure 2.7 for $T = 20\, ^\circ\text{C}$ and $T = 40\, ^\circ\text{C}$. An excellent match between the calculated and the experimental $T_1$ is found for $0 < \phi < 0.4$. At higher concentrations the difference is larger but within 10% of the experimental value.

**Relaxation in prepared gels**

The relaxation times of the prepared gel samples were measured after 14 days of preparation and at ambient temperature. In Table 2.2 the results are summarized together with $T_1$ and $T_2$ for water, methanol, mixtures of water and methanol, and TMOS, which are substances involved in the sol-gel reaction. The longitudinal relaxation in the gels appeared to be mono-exponential. For the lowest initial concentration of TMOS ($\phi_T^{g} = 0.05$), $T_1$ is almost equal to that of water, but decreases with increasing concentration. Between $\phi_T^{g} = 0.30$ and $\phi_T^{g} = 0.50$, $T_1$ is constant (about 1.70 s). The reduction of $T_1$ of the wet gels with respect to $T_1$ of water is thus limited to about 50% for the range of concentrations considered.

The CPMG data were analyzed using the inversion routine CONTIN. The $T_2$ spectra of water and TMOS appeared to be mono-exponential. Subsequent fitting of the data with a single exponent yielded a $T_2$ of 1.66 s and 1.33 s for water, respectively, TMOS (with $G = 100\, \text{mT/m}$ and $\Delta \tau_E = 7.2\, \text{ms}$). The differences between $T_2$ and $T_1$ for water and TMOS are explained by the effect of molecular diffusion (see Section 2.3.2).

The gel $T_2$ spectra and the $T_2$ spectra of water/methanol showed a multi-exponential behavior with well-separated components within the range of the inversion. Additionally,
2.4. Results and discussion

**Table 2.2:** Results of the NMR calibration measurements for the gels (at $T = 22 \pm 2 \, ^\circ\text{C}$) and liquids (at $T = 25 \pm 1 \, ^\circ\text{C}$). $T_2$ was measured with an inter-echo time of 7.2 ms and with a pulsed read-out gradient $G = 100 \, \text{mT/m}$. $\phi_g^T$ is the volume fraction of TMOS mixed with water. $R$ is the water/methanol molar ratio, and $R_{eq}$ is the equivalent molar ratio in case of full hydrolysis and condensation.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$R$</th>
<th>$T_1$ [s]</th>
<th>$T_2$ [s]</th>
<th>Exponent First</th>
<th>Exponent Second</th>
<th>Exponent Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>3.26</td>
<td>1.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMOS</td>
<td>3.57</td>
<td>1.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td>4.09</td>
<td></td>
<td>0.42</td>
<td>1.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>water-methanol</td>
<td>8.97</td>
<td>2.54</td>
<td>0.195</td>
<td></td>
<td>-</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>3.36</td>
<td>2.29</td>
<td>0.141</td>
<td></td>
<td>-</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>2.24</td>
<td>2.32</td>
<td>0.070</td>
<td>0.70</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.49</td>
<td>2.47</td>
<td>0.060</td>
<td>0.73</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>2.95</td>
<td>0.055</td>
<td>0.46</td>
<td>1.28</td>
<td></td>
</tr>
</tbody>
</table>

**Gel** ($\phi_g^T$) | $R_{eq}$ | $T_2$ [s] | Exponent First | Exponent Second | Exponent Third |
<table>
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<tr>
<td>0.05</td>
<td>38.6</td>
<td>2.71</td>
<td>0.120</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>0.10</td>
<td>18.0</td>
<td>2.34</td>
<td>0.065</td>
<td>0.18</td>
<td>0.53</td>
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<tr>
<td>0.15</td>
<td>11.2</td>
<td>2.15</td>
<td>0.045</td>
<td>0.24</td>
<td>0.58</td>
</tr>
<tr>
<td>0.20</td>
<td>7.7</td>
<td>2.03</td>
<td>0.038</td>
<td>0.31</td>
<td>0.62</td>
</tr>
<tr>
<td>0.25</td>
<td>5.7</td>
<td>1.90</td>
<td>0.029</td>
<td>0.30</td>
<td>0.66</td>
</tr>
<tr>
<td>0.35</td>
<td>3.3</td>
<td>1.70</td>
<td>0.027</td>
<td>0.22</td>
<td>0.66</td>
</tr>
<tr>
<td>0.40</td>
<td>2.6</td>
<td>1.69</td>
<td>0.026</td>
<td>0.29</td>
<td>0.64</td>
</tr>
<tr>
<td>0.50</td>
<td>1.6</td>
<td>1.70</td>
<td>0.029</td>
<td>0.32</td>
<td>0.66</td>
</tr>
</tbody>
</table>

A discrete tri-exponential fit was performed on the spin-echo trains to quantify the exponents. A dominant component was found in the order of tens of milliseconds for each gel that appeared to be almost independent on the read-out gradient used, so that in this case the observed $T_2$ is not influenced by molecular diffusion. Between $\phi_g^T = 0.25$ and $\phi_g^T = 0.50$ $T_2$ is almost constant (about 30 ms). The multi-exponential relaxation behavior of the aqueous samples is not trivial. It clearly indicates that the different hydrogen species exhibit different relaxation rates. The mechanisms that cause the multi-exponential relaxation are discussed below.

The hydrolysis reaction of TMOS leads to the formation of methanol. In the case of full hydrolysis and complete condensation, the molar water/methanol ratio can be inferred from the initial water/TMOS ratio. This is denoted as the equivalent ratio $R_{eq}$ and is given in Table 2.2 for the calibration gel samples. It is noted, however, that condensation for these samples is not complete, since this would lead to a dense glass and separation of the liquids from the gel, which is not the case for the calibration gels. Water/methanol mixtures are known to exhibit anomalous thermodynamic properties, such as mixing entropy, viscosity etc. [68]. At the molecular scale the mixing of methanol with water is incomplete leading to complex solution structures. This is due to the chain-like and
ring-like alignment of the methanol molecules surrounding the water molecules [69]. The structure is caused by hydrogen bonds on the one hand and repulsion among the methyl groups and water on the other.

Additionally, a rapid exchange among the hydrogen nuclei from methanol hydroxyl groups and water molecules occurs. This explains the rather different relaxation spectra of the mixtures compared to either pure water or methanol. $T_1$ for a solution (1:1 volume ratio or 1:2.24 mole ratio) of methanol in water was measured to be 2.32 s at 25 °C, whereas for water $T_1 = 3.26$ s, and for methanol $T_1 = 4.09$ s. The $T_2$ spectra for water, methanol and the mixture (obtained with a CONTIN inversion of the CPMG data) are shown in Figure 2.8. Water shows a peak near $T_2 = 1.66$ s. Methanol has a bimodal distribution, which is attributed to the different relaxation mode of the methyl group protons and the hydroxyl protons, respectively. The area of the peaks indicates the relative proton density of the species (in analogy with spectroscopic frequency or chemical shift measurements [70]). Interestingly, in the mixture a dominant peak arises near 70 ms, while the peaks at higher times resemble the methanol peaks. Based on the relative intensities of the peaks and the known composition, it follows that (most of) the water hydrogen nuclei have a shifted relaxation mode towards a much lower time of about 70 ms. The hydrogen exchange among the hydroxyl species has an influence on the relative intensities and times as well. The separate relaxation behavior of the hydrogen species was confirmed by chemical shift-$T_2$ measurements (not presented here). $T_1$ and $T_2$ for water/methanol mixtures of various ratios are listed in Table 2.2.

It is concluded that the strong contrast in $T_2$ of the gels with respect to pure water or TMOS is caused by the complex structure of methanol/water solutions, since the liquids constitute the main part of the wet gels. Additional shortening of $T_2$ and $T_1$ is due to the geometrical confinement of the liquids in the gels and interaction of the liquids with
the silica structure [71, 72], respectively. The dominant component in the $T_2$-spectra is attributed to the water molecules. In the two-phase bulk experiments the focus will be on this component when analyzing the relaxation behavior of the aqueous phase.

### 2.4.2 Two-phase bulk systems

**NMR images**

The 2D images of the reactive bulk systems were analyzed after each experiment. Qualitatively the images show the same features for each initial concentration and temperature. First of all, the oleic and aqueous phase are always clearly separated due to the contrast in $T_1$ (see Figure 2.9).

The interface between the two phases is curved due to the attraction of the oleic phase to the Teflon. Every time step the intensity appears to be uniform within each phase, which means that in the oleic phase the concentration gradients of TMOS are small (or at least cannot be detected). In the aqueous phase the intensity remains almost constant during the experiment. The gelation lowers the $T_1$, but this is too weak to produce a significant increase in intensity. The images further reveal that during the experiment the interface moves upward, so that the phase volumes change, indicating the mass transfer of TMOS from one phase to the other. The mass transfer is complete after several hours depending on the initial TMOS concentration in $n$-hexadecane. Then the images remain unchanged during the rest of the experimental time (up to 18 hours) except for some minor changes in the interfacial shape in some of the experiments. The latter is possibly due to the effect of gelation, but this was not investigated further.

![Fig. 2.9: $T_1$-weighted 2D TSE images of a vertical slice of the two-phase bulk system at 25 °C. Initially the upper phase consists of $n$-hexadecane/TMOS mixture ($\phi_0 = 0.40$), and the lower phase is demineralized water. (left) First frame at $t = 8$ minutes after injection. (right) Final frame after 14.5 hours.](image-url)
2. Coupled mass transfer and sol-gel reaction in a two-phase bulk system

Table 2.3: Overall mass transfer coefficient $\kappa$ (hours$^{-1}$) of the two-phase bulk experiments. $\phi_0$ is the initial TMOS volume concentration.

<table>
<thead>
<tr>
<th>temperature</th>
<th>$\phi_0 = 0.20$</th>
<th>$\phi_0 = 0.40$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>0.44 ± 0.02</td>
<td>1.02 ± 0.04</td>
</tr>
<tr>
<td>35 °C</td>
<td>0.46 ± 0.03</td>
<td>1.14 ± 0.04</td>
</tr>
<tr>
<td>45 °C</td>
<td>0.43 ± 0.01</td>
<td>1.52 ± 0.09</td>
</tr>
</tbody>
</table>

Concentration profiles

The 1D (vertical) $T_1$ profiles of the bulk systems were used to monitor the concentration of TMOS in $n$-hexadecane. An example of the profiles obtained from one of the experiments is presented in Figure 2.10. At each time step the profile consist of two plateaus separating the oleic from the aqueous phase. Similarly to the 2D images the $T_1$ appears to be uniform within each phase.

These findings are also consistent with the visual observation that a slight degree of gravity-induced convection is found, especially in the aqueous phase. Density gradients can therefore not be sustained and mixing is enhanced. The interface is now indicated by the decrease in $T_1$ at a certain position $z$. The fronts are rather wide due to the curved interfaces and the fact that the measurements are one-dimensional. Since $T_1$ is almost uniform at each time step the average concentration of TMOS is determined using the averaged $T_1$ of the oleic phase. The results are shown in Figure 2.11. All data sets show a certain degree of scattering and the accuracy of the concentration determination is about ± 0.02.

For the temperatures considered and in the case of an initial concentration of 0.40, the mass transfer is complete after about 6 hours. The experiments with initial concentration of 0.20 show a similar trend, but the mass transfer is complete after about 10 hours. A sharp indication is not possible due to the gradual transition. The concentration profiles show an exponential decay, therefore the concentration data were fitted with a first-order exponential function, i.e.

$$\phi(t) = \phi_0 \exp(-\kappa t),$$

where $\kappa$ represents an overall mass transfer coefficient. The obtained coefficients are listed in Table 2.3. For the initial concentration of 20 vol% TMOS in $n$-hexadecane the mass transfer rate is about 0.5 hours$^{-1}$ and does not depend significantly on temperature. The 40 vol% experiments have higher transfer rates of at least 1.0 hours$^{-1}$, which are also increasing with temperature.

Relaxation of the aqueous phase

With respect to the aqueous phase $T_1$ was not analyzed further. Instead, the CPMG data were analyzed in detail (the procedure is shown in Figure 2.2). For each experiment the data were inverted with the CONTIN routine. Due to the uniformity of the phases at a specific time step the $T_2$ spectra were derived from the mean signal decay of the aqueous phase. This was done by averaging the part of the 1D signal profiles related to
2.4. Results and discussion

Fig. 2.10: 1D $T_1$ profiles of the bulk system in the vertical direction. A sharp contrast in $T_1$ enables to clearly distinguish the phases. The left-hand side of each profile represents the aqueous phase, the right-hand side represents the oleic phase. The initial TMOS fraction is 0.4, and the temperature is 35 °C. The profiles are given for various time steps.

Fig. 2.11: Average concentration of TMOS in the oleic phase as a function of time for different temperatures. (left) $\phi_0 = 0.40$, (right) $\phi_0 = 0.20$. 
the aqueous phase for each echo in the spin-echo train. The \( T_2 \) spectra as a function of time are shown in Figure 2.12 for one of the experiments, but all experiments showed a similar trend.

![Fig. 2.12: \( T_2 \) spectra of the aqueous phase (averaged) as a function time for the experiment with initial TMOS fraction of 0.4 and temperature of 25 °C. The \( T_2 \) spectra are obtained using the CONTIN routine.](image)

A dominant component is initially found near the \( T_2 \) for water but rapidly moves to shorter times (see also Figure 2.13). This is caused by the introduction and hydrolysis of TMOS in the water phase and the subsequent formation of methanol. Additionally, the aggregation of the silicic acid leads to a growing silica surface interaction with the fluid components. The dominant \( T_2 \) becomes stationary or even becomes slightly longer (depending on the temperature), after which \( T_2 \) becomes shorter again and levels off after several hours. The leveling off indicates that the gel reaction has ended and that no major changes in the aqueous phase occur after the minimum in \( T_2 \) occurs. A slight increase of \( T_2 \) following the minimum is attributed to further condensation which leads to an increasing water-methanol ratio. Secondly, during aging a decrease in the specific surface area of the silica is caused by silica dissolution and redeposition in crevices and necks of the network [47]. This way the effect of surface relaxation and the effect of methanol on \( T_2 \) is slightly reduced. The spectra inherently produce Gaussian-like peaks, therefore the dominant component was fitted with a Gaussian (not shown here) in order to quantify its position on the \( T_2 \) axis. A detail of the resulting dominant \( T_2 \) profile is shown in Figure 2.13. Like the calibration samples the \( T_2 \) is virtually independent on the magnetic gradient strength. The final \( T_2 \) is slightly longer (at 25 °C) than the values obtained from the calibration samples.

The point at which \( T_2 \) reaches the minimum was found to be strongly dependent on temperature and initial TMOS concentration. Although the minimum is not sharply defined a geometrical construction was manually applied in the graphs for each experiment.
Fig. 2.13: Detail of the dominant $T_2$ component in the aqueous phase as a function of time for the experiment with initial TMOS fraction 0.4 and temperature 25 °C. The $T_2$ was measured using three different read-out gradient strengths as indicated in the legend. The lines in the graph indicate the construction used to find the time at which the $T_2$ reaches a plateau.

Fig. 2.14: Gel times for the bulk experiments obtained from the NMR and tilting test tube measurements. The initial TMOS concentration in the $n$-hexadecane is shown in the legend. The error bars shown hold for all data sets.
to find the points at which the minima occur. The resulting transition time (with an accuracy of about 30 minutes) was subsequently compared to the gel times obtained from the tilting test tube experiments (as demonstrated in Figure 2.14). A good agreement is found between the gel times and the times at which the minimum $T_2$ (or plateau) occurs. The leveling-off time in $T_2$ therefore appears to be an adequate indication for the gel transition time in these experiments.

### 2.5 Conclusion

In binary mixtures of TMOS and $n$-hexadecane the longitudinal relaxation time $T_1$ increases monotonically with the concentration of TMOS and with temperature. The measurement of $T_1$ proves to be a robust method to determine concentrations in a non-intrusive manner. The prepared gels showed a significant decrease in the transverse relaxation time $T_2$ compared to either water, TMOS or methanol. The short $T_2$ component is related to the water hydrogen nuclei, whereas the longer components can be attributed to methanol. The shortening of the water $T_2$ component is due to the interaction of water with methanol. An additional decrease of the relaxation times is caused by the geometrical confinement in the gel structure, and the interaction of the fluid with the silica surface.

Through the measurement of $T_1$ the concentration of TMOS in $n$-hexadecane was determined dynamically during the experiments with an accuracy of about 2 vol%. Both the $T_1$-weighed 2D images as the $T_1$ profiles revealed that the oleic and the aqueous phase were uniform in terms of $T_1$ at each time step measured during the reactive mass transfer. Significant concentration gradients were therefore not observed, which means that the mass transfer within each phase is enhanced by convective mixing, and is not due to diffusion only. After the phases are brought in contact the average concentration of TMOS in the oleic phase decreases exponentially. The rate is rather insensitive to temperature (within the range of 25–45 °C), but is sensitive to the initial concentration of TMOS. In case of an initial concentration of TMOS of 40 vol% the rate is at least two times higher compared to the lower initial concentration of 20 vol%. The gel point of the aqueous phase is indicated by the minimum (or plateau) in $T_2$, which appears after several hours when the fluids are brought in contact. The gel time decreases with increasing temperature and with increasing initial TMOS concentration.
Chapter 3

Interfacial effects during reactive transport*

The mass transfer coupled with hydrolysis and gelation in the aqueous phase gives rise to an intriguing motion of the interface between both phases. This phenomenon was analyzed in detail both theoretically and experimentally. The theory was developed assuming quasi-static conditions and provides a non-linear second order boundary value problem, which was treated numerically. Magnetic Resonance Imaging (MRI) experiments are used to quantify the fluids in the oil and water phases and capture the interface profiles between the oil and the water phases at different time intervals. An excellent fit of the theoretical interface profiles to the experimental ones at various times reveals that the interfacial tension increases gradually during the extent of the mass transfer.

3.1 Introduction

The coupled mass transfer and gel reaction of TMOS in two-phase bulk systems were studied using Magnetic Resonance Imaging (MRI). Nuclear magnetic relaxation times ($T_1$ and $T_2$) were used to determine the concentration of TMOS in oil and to monitor the progress of gelation (see Chapter 2). The images revealed that the reactive mass transfer in these systems gives rise to an intriguing motion of the interface between the oleic and the aqueous phases. Figure 2.9 shows two MRI images of a two-phase bulk system within a small Teflon vial. Initially, the oleic phase, consisting of n-hexadecane, is mixed with TMOS at a concentration of 40 vol%. During the experiment the TMOS gradually transfers to the aqueous phase, while the volumes of the phases change and, as a result, the interface moves upwards. In addition, the shape of the curved interface and the contact angles at the vial material show subtle changes during the reactive mass transfer, suggesting gradual changes in interfacial tension (IFT). The main question is whether the IFT increases or decreases during the process. This is also of interest in light of the application of the chemical. For example, when a mixture of TMOS and oil is injected in a water-saturated porous material the IFT determines the capillary forces and hence the displacement and distribution of the fluids.

Interfacial tension between organic liquids and water has been extensively studied in the past, both experimentally and theoretically [73–77]. Also, the IFT between mixtures of organic compounds and water has been investigated [78]. Common methods to measure surface or interfacial tension are either based on a force balance, using a Wilhelmy plate [79] or a du Noüy ring [80], or on visualization of droplet surfaces, such as the pendant

* Adapted from Castelijns et al., Colloid Surf. A, in press (2007)
3. Interfacial effects during reactive transport

3.1 Physical model

3.1.1 Mass transfer and chemical reactions

Consider a cylindrical container with radius \( R \) in which two liquid phases are situated. The system is depicted in Figure 3.1. Phase 1 initially consists of water, and phase 2 consists of a solution of TMOS in oil with an initial volume concentration \( \phi_T^0 \). From the
3.2. Physical model

moment the phases are put together the TMOS partitions between both phases and in
the aqueous phase it undergoes a heterogeneous reaction.

The MRI measurements have shown that during the mass transfer within each phase
the chemicals are well-mixed, and no significant density or concentration gradients exist
[88]. Theoretically, the depletion of TMOS in the oleic phase at the interface and the
downward flux of TMOS in the aqueous phase give rise to density gradients. However,
the density gradients are diminished by convection due to the effect of gravity. The mass
transfer is therefore assumed to be fast compared to the chemical reactions. The overall
flux of the TMOS between the two phases is controlled by the rate of hydrolysis and the
solubility of TMOS in water.

The densities of the oleic and the aqueous phase are $\rho_o$ and $\rho_w$, respectively, and $\rho_w > \rho_o$. The density of the oleic phase is a function of the TMOS concentration $\phi_T$ and is simply given by

$$\rho_o = \phi_T \rho_T^* + (1 - \phi_T) \rho_o^*,$$

where $\rho_T^*$ and $\rho_o^*$ are the densities of the pure TMOS and oil components, respectively. Further, we assume the interface between the liquids has an axisymmetric shape. Due
to interfacial tension between the liquids and between the liquids and the solid wall, in
general, the interface will be curved. The shape of the interface between the phases
is given by the height $h(r, t)$. The volumes of the oleic and aqueous phase are $V_o(t)$,
respectively, $V_w(t)$. In the course of time the volume $V_w(t)$ increases and the volume $V_o(t)$
decreases as a result of the mass transfer.

A conceptual model is proposed to describe the overall flux of TMOS between the
phases. The change in the total number of TMOS molecules $n_t$ in the system as a
function of time is described by the following kinetic equation

$$\frac{dn_t}{dt} = \frac{dn_o + n_w}{dt} = -kn_w,$$

where $n_o$ and $n_w$ are the number of TMOS molecules in the oleic, respectively, the aqueous
phase and $k$ is the rate of hydrolysis. The ratio between $n_o$ and $n_w$ at each instant is
determined by the solubility of TMOS in both phases. In the oleic phase the mixing is
ideal. In the aqueous phase the solubility is determined by the concentration of methanol.
The balance of TMOS between both phases is driven by the chemical potential, which is
derived from the free energy of the system. By equating the chemical potential of TMOS
in the oleic phase to the chemical potential of TMOS in the water phase the following
partitioning expression is obtained (see Appendix B)

$$\frac{n_w}{n_w + m_w} = \frac{n_o}{n_o + m_o} \exp \left( -\varepsilon(n_m) \frac{R_g T}{m_w} \right),$$

where $m_w$ is the total number of water, methanol and silicic acid molecules, $m_o$ is the
number of hydrocarbon molecules, $R_g$ is the gas constant, $T$ is the temperature and $\varepsilon$ is
an interaction parameter which depends on the methanol concentration $n_m$. Although
the exact choice of $\varepsilon(n_m)$ is still arbitrary, the parameter should decrease with an increasing
value of $n_m$ and vice versa. As a first-order approximation, the parameter $\varepsilon$ is chosen as

$$\varepsilon = \varepsilon_0 \left[ 1 - \alpha \frac{n_m}{m_w(0)} \right],$$

where $m_w(0)$ is the initial number of water molecules. This choice of $\varepsilon$, along with
the assumption of ideal mixing in the oleic phase, implies that the interface
between the phases has a constant density and a contact angle of zero. In
general, these assumptions may be invalid, and the interface shape and
contact angle should be determined by a more detailed model.
where $\varepsilon_0$ is the interaction parameter in absence of methanol and $\alpha$ is an arbitrary scale factor. The methanol concentration $n_m$ increases in the course of time as given by

$$n_m = 4 \int_{t_0}^{t} k n_w(\tau) d\tau = 4 [n_t(0) - n_t(t)].$$  \hfill (3.5)

The variables $n_w$ and $m_w$ in Eq. 3.3 are rewritten in terms of $n_o$ and $m_o$. Then, by rearranging Eq. 3.2 the following differential equation is obtained

$$\frac{dn_o}{dt} = -k E n_o [N - (n_o + m_o)] \left\{ (n_o + m_o) + 4\varepsilon_0 \alpha \beta En_o [N - (n_o + m_o)] \right\} \frac{ENm_o + (1 - E)(n_o + m_o)^2}{ENm_o + (1 - E)(n_o + m_o)^2},$$  \hfill (3.6)

where $E = \exp(-\varepsilon/R_g T)$, $\beta = (R_g T)^{-1}$ and $N$ is the total number of particles, which is constant. The initial value for $n_o$ is derived implicitly from Eq. 3.3 using $n_t = n_o + n_w = n_t(0)$. For convenience, we express $n_o$ in the volume fraction of TMOS in oil $\phi_T$, yielding

$$n_o = \frac{\phi_T}{1 - \phi_T} m_o.$$  \hfill (3.7)

Equation 3.6 will be solved numerically in terms of $\phi_T$ and optimized to fit the experimental data, yielding the parameters $\varepsilon_0$ and $k$. The parameter $\alpha$ is not optimized to limit the number of parameters in the optimization. The optimization is weakly sensitive to the value of $\alpha$. We choose $\alpha = \frac{1}{2}$, so that $\varepsilon$ reduces by 40 to 80% during the reactive transport given the estimated final amount of methanol. This means that the solubility of TMOS in the aqueous phase increases significantly.

### 3.2.2 Interface description

As stated in Section 3.1 the IFT analysis is based on an image analysis and optimization procedure. The image analysis yields a representation of $h(r)$ (see Figure 3.1). In order to derive the IFT from the function $h(r)$ we need to consider the energy of the interface, which depends on the IFT and gravitational forces. Our model is based on the assumption that in the two-phase systems the interface is always at a quasi-static equilibrium condition, i.e. the interface is not deformed by the upward motion, because the mass transfer and the motion are relatively slow (order of hours). More precisely, we can decouple the motion and the deformation of the interface. The energy of the interface is given by

$$E = 2\pi \int_{0}^{R} \left( \gamma_{12} r \sqrt{1 + h_r^2} + \frac{1}{2} \Delta \rho g r h_r^2 \right) dr,$$  \hfill (3.8)

where $\gamma_{12}$, $\Delta \rho = \rho_w - \rho_o$ and $g$ are the interfacial tension, the density difference, and the gravity constant, respectively. The first term is the energy due to the interfacial tension, which is proportional to the surface area of the interface; the second term is the energy due to the effect of gravity. To obtain the equation for the equilibrium we minimize the energy using the variational principle. This leads to the following second order differential equation

$$\Delta \rho g r h_r - \gamma_{12} \left( \frac{h_r}{\sqrt{1 + h_r^2}} + \frac{r h_{rr}}{(1 + h_r^2)^{3/2}} \right) = 0,$$  \hfill (3.9)
which has to be solved using the boundary conditions:

\[ h_r = \begin{cases} 
0 & r = 0 \\ 
cotan(\theta) & r = R 
\end{cases}, \]

where \( \theta \) is the contact angle at the three-phase contact.

### 3.2.3 Image analysis

We describe the image analysis procedure that we developed to derive the parameters \( \gamma_{12} \) and \( \theta \) from the MRI images of the two-phase system. The images were acquired using \( T_1 \) weighting such that the phases have the highest possible signal contrast. After selecting an appropriate region of interest for each time step the image analysis is performed to obtain a smooth interface representation, \( \tilde{h}(x_i) \), i.e. the height of the interface as a function of position \( x_i \) in the images (\( x_i \) is the horizontal coordinate of each column). Near the two-phase contact the vertical columns show a clear jump in signal. An arbitrary smooth function is fitted to the pixel values in each column. This procedure results in a smooth representation of the interface. For convenience, we choose the following inverse tangent function

\[ f(z) = A \tan^{-1} \left( \frac{z - z_0}{\xi} \right) + B, \]

where \( A, z_0, \xi \) and \( B \) are the amplitude, the inflection point, the steepness coefficient and the offset, respectively. Finally, exploiting the cylindrical symmetry of the problem, the horizontal center coordinate of \( \tilde{h}(x_i) \) is determined, and the profile is split into two parts. The left-hand-side and right-hand-side part of the profile are then regarded as two separate axisymmetric representations of the interface, i.e. \( \tilde{h}_L(r) \) and \( \tilde{h}_R(r) \), respectively.

### 3.2.4 Optimization procedure

The second aspect of the IFT determination consist of the true optimization, which is an iterative process. Starting with an initial guess of the parameters \( \gamma_{12} \) and \( \theta \) the shape function \( h(r) \) is determined by solving the boundary value problem (BVP) given in Section 3.2.2. The calculated function \( h(r) \) is simultaneously compared with the values of both \( \tilde{h}_L(r) \) and \( \tilde{h}_R(r) \). This way the method is rather insensitive to image distortions. Based on a least-square method the process is repeated automatically with improved values for \( \gamma_{12} \) and \( \theta \). After about 200 iterations a satisfactory match of the calculated \( h(r) \) with \( \tilde{h}_L(r) \) and \( \tilde{h}_R(r) \) is obtained.

### 3.3 Experimental section

#### 3.3.1 Materials

Tetra-methyl-ortho-silicate, \( \text{Si(OCH}_3)_4 \), was obtained from Aldrich (\( \geq 99\% \) pure). It was dissolved in \( n \)-hexadecane (\( n\text{-C}_{16}\text{H}_{34} \)), obtained from Merck (\( \geq 99\% \) pure), to form the oleic phase. For the aqueous phase we used double-demineralized water. Methanol (Merck, 99\%
pure) was mixed with the water in one of the experiments. This was done to determine whether methanol would have an effect on both the mass transfer and the IFT. The two-phase bulk experiments were performed using cylindrical Teflon vials with an inner diameter of 18 mm. In each experiment 2.5 ml of water and 2.5 ml of TMOS/\textit{n}-hexadecane were placed in the vial. The initial volume fractions of TMOS were 0.20 or 0.40.

3.3.2 MRI experiments

The MRI imaging and relaxation time measurements were done using a 4.7 Tesla MRI scanner. The setup consists of a super-conducting magnet (Oxford Instruments, Oxon, UK) with a vertical, narrow-bore insert (Doty, Columbia, USA). The temperature of the samples is controlled by the sample holder, in which a fluorocarbon fluid (Galden™ HT135, manufactured by Solvay Solexis) is circulated. The fluid is invisible to the NMR set-up and the temperature can be controlled between 10 and 65 °C with an accuracy of about 1 degree.

A Turbo Spin Echo (TSE) sequence [63] was used to acquire the images. A train of 180° RF pulses is used to produce a train of phase-encoded echoes, generating one spatial dimension. The second spatial dimension is obtained due to the presence of a frequency encoding gradient between the 90° pulse and the first 180° pulse. This gradient is also switched on during the acquisition of the echo signal, and is therefore referred to as read-out gradient. The slice selection gradient was applied perpendicular to the read-out direction, yielding a vertical slice with a thickness of about 4 mm. The resolution of the images was set at 128 x 128 pixels with a pixel size of 234 x 234 µm². The turbo factor in the TSE sequence was 16. No significant blurring or ghosting was observed in the images. The magnetic susceptibility of water and \textit{n}-hexadecane is $-9.0 \times 10^{-6}$, respectively, $-8.0 \times 10^{-6}$ [67]. At 4.7 Tesla the resulting frequency mismatch is about 200 Hz. With respect to the applied read-out gradient of 4.3 kHz mm$^{-1}$, susceptibility artifacts at the interface between \textit{n}-hexadecane and water are insignificant. The acquisition time of each image was 2.5 minutes, and the measurement was repeated about every 10 to 15 minutes.

3.3.3 Tensiometer

The tensiometer used was a KSV Sigma 701 (KSV Instruments, Finland). A du Noüy ring was mounted on the balance. The software of the apparatus derives the IFT from the maximum pull using the correction of Huh and Mason [89] for which the densities of the phases are needed as input parameters. The densities of the phases could not be monitored during the IFT measurements. The density of the oleic phase was set to that of pure \textit{n}-hexadecane, which is 0.771 g cm$^{-3}$, and the density of the aqueous phase was set to that of pure water, which is 0.998 g cm$^{-3}$ [67].

The samples containing the two phases are different from the samples used in the MRI experiments. Here the container is a glass beaker with an inner diameter of 56 mm. The initial volume of each phase was chosen as 30 ml in yielding a column height of each phase of about 12 mm.
3.4 Results and discussion

3.4.1 MRI analysis and optimization

Mass transfer

In the experiments the volume fraction $\phi_T$ of TMOS in $n$-hexadecane during the mass transfer was derived from NMR relaxation time $T_1$ (see Chapter 2). In Figure 3.2 the volume fraction (of TMOS in oil) versus time is shown for three different experiments where the initial volume fraction of TMOS in oil was 0.40. In all cases the determined concentration $\phi_T$ starts near the initial concentration of the mixture, after which it decreases almost completely to zero within several hours. The density of the oleic phase, which is needed in the IFT analysis, is calculated using Eq. 3.1. For TMOS the density $\rho_T^*$ is 1.032 g cm$^{-3}$ [67]. For the aqueous phase the density $\rho_w$ remains approximately constant at 1.0 g cm$^{-3}$ also during the mass transfer and gel reactions.

The experimental concentration profiles were fitted with numerical solutions of the mass transfer model (see Section 3.1). For each experiment the parameters $\varepsilon_0$ and $k$ were obtained by optimizing the solution of the model. The fit results are shown in Figure 3.2 for part of the experiments. A good agreement is found between the experimental data and the model fits. The resulting parameters $\varepsilon_0$ and $k$ are given in Table 3.1. Although the dependence of $\varepsilon$ on $n_m$ was arbitrarily chosen as described in Section 3.1, the model appears to be adequate and yields consistent results. The values of $\varepsilon_0$ are on the order of several kJ mol$^{-1}$. The values of $k$ are on the order of $10^{-4}$ to $10^{-3}$ s$^{-1}$. The experiment with the extra methanol in the aqueous phase yields a relatively low reaction rate, i.e. $k = $
Table 3.1: Interaction parameter $\varepsilon_0$ and reaction constant $k$ derived for the two-phase bulk experiments. $\phi^0_T$ is the initial TMOS volume concentration. In one experiment at 25 °C the aqueous phase initially contained 50 vol% methanol (MeOH).

<table>
<thead>
<tr>
<th>$T$ [°C]</th>
<th>$\varepsilon_0$ [kJ mol$^{-1}$]</th>
<th>$k$ [$10^{-4}$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi^0_T = 0.20$</td>
<td>$\phi^0_T = 0.40$</td>
<td>$\phi^0_T = 0.20$</td>
</tr>
<tr>
<td>25 (MeOH)</td>
<td>$6.1 \pm 0.4$</td>
<td>$2.7 \pm 0.2$</td>
</tr>
<tr>
<td>35</td>
<td>$6.3 \pm 0.6$</td>
<td>$3.2 \pm 0.2$</td>
</tr>
<tr>
<td>45</td>
<td>$6.3 \pm 0.5$</td>
<td>$4.6 \pm 0.4$</td>
</tr>
</tbody>
</table>

1.36 ± 0.05 × 10$^{-4}$ s$^{-1}$, compared to the experiments without methanol. A higher order reaction term, which includes the concentration of methanol, would be more appropriate in Eq. 3.7, but this is left for future studies.

IFT determination

It is noted that the IFT determination using the model in Section 3.2 is not valid for the images related to the gelled state of the aqueous phase. After gelation the gravity forces are not able to diminish the degree of curvature while a density difference between both phases still exists. However, it was observed that the shape of the interface still changes after gelation in some of the experiments, which is attributed to aging effects of the gelled phase. Therefore, the IFT determination is only done using part of the images belonging to the non-gelled systems.

Figure 3.3 shows the results of the image analysis and interface optimization for one of the experiments at 25 °C with respect to three different time steps. The discrete representation of the interface obtained from the image analysis is shown by the symbols. The solid curves indicate the calculated shapes resulting from the optimization. As can be observed, for all three time steps the fit of the calculated shapes is excellent with respect to the discrete profiles. In this case, the first frame at $t = 0.1$ hours results in an IFT of 11 mN m$^{-1}$. At $t = 0.8$ hours, when the interface has moved upwards considerably, the IFT has increased to 13 mN m$^{-1}$. At $t = 5.8$ hours, when the mass transfer is complete, but prior to the gel point, the IFT has increased to 24 mN m$^{-1}$. The system then consists of almost pure $n$-hexadecane in the oleic phase and a gelling solution in the aqueous phase.

It is noted that, although the fit of the interfaces is accurate, the method is sensitive to the image quality and to the density parameters. The scale of the MRI images needs to be accurate, which means that the magnetic gradients need to be well calibrated. A scale error in the $z$-direction of 5% results in a systematic error of the IFT of about ± 2 mN m$^{-1}$. An uncertainty in $\Delta \rho$ of 5% yields an uncertainty in the IFT of about ± 1 mN m$^{-1}$. The smoothness of the interface captured by the image analysis is of great importance for the accuracy; in case the interface contains some deviating points, as a result of blurring or low signal-to-noise ratio in the image, the optimization results in significant errors in the IFT. This effect was observed in some of the images, but is difficult to quantify. A validation experiment was performed on a water sample contained in a glass vial. With the
3.4. Results and discussion

same resolution and MRI parameters as in the two-phase experiments the surface tension (SFT) was determined four times. The average SFT at room temperature was $74 \pm 3 \text{ mN m}^{-1}$. An additional MRI image was obtained with twice the resolution, a higher number of signal averages and a turbo factor of 1. In this case the SFT was $71 \pm 1 \text{ mN m}^{-1}$, which agrees well with literature [67]. Furthermore, the IFT of a $n$-hexadecane/water sample was measured at room temperature with the same resolution and MRI parameters as the other two-phase systems. The average value derived from four images was $47 \pm 7 \text{ mN m}^{-1}$.

**Effect of temperature and concentration**

In the left-hand graph of Figure 3.4 the IFT is shown as a function of time for the experiments with the initial volume fraction of TMOS of 0.40. Despite the scatter, which is especially observed for the measurement at 45 °C, it is obvious that the IFT in the systems without initial methanol starts around $10 \text{ mN m}^{-1}$ and increases gradually during the first two hours to at least $20 \text{ mN m}^{-1}$.

A clear effect of temperature on the IFT is not found in the temperature range considered. Interestingly, the IFT in the system with the initial methanol present in the aqueous phase starts at $8 \text{ mN m}^{-1}$ and remains constant in the first three hours, after which it increases slowly to about $15 \text{ mN m}^{-1}$. Although the experiments without the initial methanol had similar concentration decays of TMOS in $n$-hexadecane as a function of time (see Figure 3.2), the concentration profile for the experiment with methanol was different. The latter shows a lower mass transfer rate. On the whole, the presence of additional methanol in the aqueous phase lowers the IFT.
A similar analysis was done on the images obtained from the experiments where the initial volume fraction of TMOS was 0.20. The IFT as a function of time is shown in the right-hand graph of Figure 3.4 for three different temperatures. Again the graphs show a significant amount of scatter. For all temperatures the first image yields an IFT around 20 mN m$^{-1}$. The values for 25 °C appear to be fluctuating slightly below 20 mN m$^{-1}$ in the initial two hours, after which the IFT approaches an average value of 21 mN m$^{-1}$. The measurement done at 35 °C yields also fluctuating IFT values, initially below 20 mN m$^{-1}$, and for later times above 20 mN m$^{-1}$. A clear difference between the results for the previous temperatures and the results for 45 °C is found for this volume fraction. After the first acquisition, the IFT fluctuates around 15 mN m$^{-1}$.

### 3.4.2 IFT from the tensiometer

A series of IFT measurements of the two-phase system was performed at room temperature. The initial volume fraction of TMOS in the oleic phase was 0.40. Figure 3.5 shows the IFT as a function of time. The initial IFT starts at 10.4 mN m$^{-1}$ after which it remains approximately constant around 10 mN m$^{-1}$ in the first 1.2 hours. The other data points, measured between 3.5 and 6.9 hours after the start, show an increasing IFT from 11.4 to 17.4 mN m$^{-1}$. The experiment was stopped after 7 hours in order to prevent gelation of the aqueous phase during the measurement.

The Huh and Mason correction factor is too small for the initial points because when TMOS is present in the oleic phase the real density difference $\Delta \rho$ is smaller than the specified difference. This means that the real IFT is slightly higher at times when there is still TMOS present in the oleic phase. The error in the correction factor is 7% for the first point but decreases as the TMOS is transferred to the aqueous phase.

The initial IFT around 10 mN m$^{-1}$ is similar to the IFT determined in the MRI experiments using the same initial concentration of TMOS. Also the ring measurement...
3.4. Results and discussion

![Graph showing interfacial tension over time.](image)

**Fig. 3.5:** Interfacial tension, measured at room temperature with the ring tensiometer, as a function of time. The initial volume fraction of TMOS was 0.40.

shows an increasing IFT during the reactive mass transfer, although the increase appears to be delayed and smaller compared to the MRI experiments.

3.4.3 Discussion

The IFT between the oleic phase and aqueous phase is always lower than the IFT between pure water and \( n \)-hexadecane. The effect of TMOS in the oleic phase on the IFT with respect to pure water can be inferred from the first data point of each experiment. The IFT appears to decrease with increasing TMOS concentration in the oleic phase. However, when the mixture of TMOS and \( n \)-hexadecane is brought in contact with water, the water composition changes in the course of time due to the reactive transfer of TMOS. The effect of methanol in the aqueous phase is to lower the IFT significantly. It is known that the presence of alcohol in aqueous solutions lowers both the surface tension with respect to the vapor or the interfacial tension with respect to organic liquids [90, 91]. In general, upon solving additional compounds in either the oleic or aqueous phase the IFT will decrease with respect to pure water against the pure organic liquid, provided that the solutes exhibit an excess surface concentration with respect to the bulk phases [92]. In the two-phase systems described above both TMOS and methanol adsorb to a certain extent at the interface. The effect of decreasing concentration of TMOS in the oleic phase on the IFT during the mass transfer is dominant compared to the increasing concentration of methanol and other reaction products in the aqueous phase.
3.5 Conclusion

The mass transfer of TMOS in a two-phase bulk system, from the oleic to the aqueous phase, gives rise to a moving interface between the phases. Experiments were previously done using MRI to characterize the mass transfer and gel reactions. In this chapter, the MRI images were analyzed in detail. In each image the interface was identified through an image analysis procedure. By optimizing and matching the solution of a calculated model interface, assuming quasi-static conditions, the interfacial tension was determined. The interfacial tension in the two-phase system increases during the reactive mass transfer, which is clearly observed in the experiments with the high initial TMOS fraction of 0.40. The change in IFT is less pronounced in the experiments with the lower initial TMOS fraction of 0.20. A verification experiment was done, with an initial TMOS concentration of 0.40, using a ring tensiometer. The trend of increasing IFT during the mass transfer was found with both methods.
Chapter 4

The effect of pH on mass transfer and gelation*

In the experiments, described in this chapter, TMOS was dissolved in a mineral oil and placed together with heavy water (D$_2$O) in small cylinders. The transfer of TMOS from the oleic phase to the aqueous phase was monitored through NMR relaxation time measurements of hydrogen in the oleic phase, while the rate of gelation was measured through NMR relaxation time measurements of deuterium in the aqueous phase. The temperature, the initial concentration of TMOS and the type of buffer in the aqueous phase were varied in the experiments. The mass transfer is driven by the rate of hydrolysis, which increases with temperature. The hydrolysis rate is the lowest at a neutral pH and is the highest at a low pH. In the aqueous phase a sharp decrease in the transverse relaxation time ($T_2$) of $^2$H is observed which is attributed to the gel reaction. The plateau in $T_2$ indicates the gel transition point. The gel rates increase with increasing temperature and increasing concentration, and are the highest at a neutral pH.

4.1 Introduction

As described in Chapters 2 and 3, the mechanisms of the coupled mass transfer and gelation process of TMOS were analyzed in two-phase bulk systems using dedicated NMR techniques. TMOS was dissolved in n-hexadecane and placed together with demineralized water (H$_2$O) in small cylinders. The concentration of TMOS and the temperature were varied, and their effect on the mass transfer rate and gelation time was determined.

This chapter describes the results of a second series of bulk phase experiments. The aim is to further analyse the effect of temperature, concentration, and pH on the reaction and mass transfer rates, which were not captured in the previous experiments. Since the solubility of TMOS in water plays an important role for the partitioning behavior, the formation of methanol due to hydrolysis is expected to affect the mass transfer process. The rate of both the hydrolysis and the condensation reaction is sensitive to temperature, concentration and pH (see Figure 4.1).

TMOS was dissolved in a mineral oil and placed in small cylinders together with heavy water (D$_2$O) with or without buffer. The transfer of TMOS from the oleic phase to the aqueous phase was monitored through NMR relaxation time measurements of hydrogen in the oleic phase, while the rate of gelation was measured through NMR relaxation time measurements of deuterium in the aqueous phase. The bi-nuclear NMR technique constitutes an excellent method to characterize both phases independently, and has not been

4. The effect of pH on mass transfer and gelation

Fig. 4.1: Schematic representation of the pH-dependence of hydrolysis (H), condensation (C), and dissolution (D) in an alkoxy-silane solution. In this case H₂O:Si = 1.5. After Brinker [33].

used before to monitor the reactive transport of TMOS in two-phase systems. Furthermore, the use of heavy water enables a straightforward interpretation of the relaxation time measurements of the aqueous phase. Finally, a simple model [93] was used to extract the hydrolysis rates from the experimental data.

4.2 Theoretical background

4.2.1 Mass transfer and hydrolysis

Consider a volume comprising two liquid phases (see Figure 3.1). The lower phase initially consists of heavy water, and the upper phase consists of a solution of TMOS in oil with an initial volume concentration $n_t(0)$, which corresponds to a volume fraction $\phi_T(0)$. From the moment the phases are put together the TMOS partitions into the aqueous phase where it undergoes the heterogeneous reaction. The system is relatively small (on the order of centimeters). The overall mass transfer is governed by the chemical reaction rate in the aqueous phase. Each phase is well-mixed (based on observations in previous experiments; see Chapter 2), so that diffusion or convection processes do not limit the mass transfer. A conceptual model was proposed in Chapter 3 to describe the overall flux of TMOS between the phases. The main equations and assumptions are repeated in this section.

The change in the total number of TMOS molecules $n_t$ in the system as a function of time is described by the following kinetic equation

$$\frac{dn_t}{dt} = \frac{d(n_o + n_w)}{dt} = -kn_w,$$  \hspace{1cm} (4.1)
where \( n_o \) and \( n_w \) are the number of TMOS molecules in the oleic, respectively, the aqueous phase and \( k \) is the rate of hydrolysis (where we assume full hydrolysis of the TMOS molecules). Assuming quasi-static equilibrium conditions, the ratio between \( n_o \) and \( n_w \) at each instant is determined by the solubility of TMOS in both phases through the following partitioning equation

\[
\frac{n_w}{n_w + m_w} = \frac{n_o}{n_o + m_o} \exp \left[ -\frac{\varepsilon(n_m)}{RT} \right],
\]

(4.2)

where \( m_w \) is the total number of water, methanol and silicic acid molecules, \( m_o \) is the number of hydrocarbon molecules, \( R \) is the gas constant, \( T \) is the temperature and \( \varepsilon \) is an interaction parameter which depends on the methanol concentration \( n_m \). The exact choice of \( \varepsilon(n_m) \) is arbitrary, but the parameter should decrease with an increasing value of \( n_m \) and vice versa. As a first-order approximation, the parameter \( \varepsilon \) is chosen as

\[
\varepsilon = \varepsilon_0 \left[ 1 - \alpha \frac{n_m}{m_w(0)} \right],
\]

(4.3)

where \( \varepsilon_0 \) is the interaction parameter in absence of methanol and \( \alpha \) is an arbitrary scale factor. The methanol concentration \( n_m \) increases in the course of time as given by

\[
n_m = 4 \int_0^t k n_w(\tau) d\tau = 4 \left[ n_t(0) - n_t(t) \right].
\]

(4.4)

The variables \( n_w \) and \( m_w \) in Eq. 4.2 are rewritten in terms of \( n_o \) and \( m_o \). Then, by rearranging Eq. 4.1 the following differential equation is obtained

\[
\frac{dn_o}{dt} = -k E n_o [N - (n_o + m_o)] \times \frac{(n_o + m_o) + 4\varepsilon_0 \alpha \beta E n_o [N - (n_o + m_o)]}{ENm_o + (1 - E)(n_o + m_o)^2},
\]

(4.5)

where \( E = \exp(-\varepsilon/RT) \), \( \beta = (RT)^{-1} \) and \( N \) is the total number of particles, which is constant. Equation 4.5 can be solved numerically and optimized to fit the experimental data, yielding the parameters \( \varepsilon_0 \) and \( k \). The parameter \( \alpha \) is not optimized to limit the number of parameters in the optimization. We choose \( \alpha = 1 \), so that \( E \) – and thus the solubility of TMOS in water – increases significantly during the reactive transport depending on \( \varepsilon_0 \) and given the estimated final amount of methanol (see Figure 4.2 for an example calculation of \( E \)).

### 4.2.2 NMR relaxation of deuterium in sol-gel

For a rigorous introduction to nuclear magnetic relaxation the reader should refer to Abragam [41]. In the gelling solution the deuterium nuclei are most abundant in the form of \( \text{D}_2\text{O} \) molecules. The main relaxation mechanism for deuterium nuclei (deuterons) in \( \text{D}_2\text{O} \) is due to quadrupolar interaction between the deuterons and the internal electric field gradient at the nuclei. This intramolecular relaxation is driven by molecular fluctuations, such as molecular rotation. The fluctuations are often characterized by a molecular correlation time \( \tau_c \) [41].

In the gelling solution the water molecules diffuse through the system and with a certain probability they adsorb onto or interact with the silica clusters. The molecules...
4. The effect of pH on mass transfer and gelation

Fig. 4.2: Partitioning coefficient $E$ as a function of the interaction coefficient $\varepsilon_0$ for $t = 0$ and $t = t_{\text{final}}$ (which represents complete mass transfer and hydrolysis). The calculations, using Eq. 4.3 with $\alpha = 1$, are based on a temperature of 25 °C and an initial volume fraction $\phi_T = 0.35$.

near a silica surface or adsorbed on the surface may exhibit anisotropic motion [94] or even behave "ice-like" [95].

One can assign different phases in which a molecule or nucleus resides during a certain life time [94, 96]. Each phase $i$ has a transverse relaxation time $T_{2,i}$ brought about by an effective correlation time $\tau_{c_i}$. The shorter $\tau_{c_i}$ the longer is $T_{2,i}$ [41]. The silica is dispersed on the scale of nanometers. Due to diffusion the water molecules distant from the silica surface will exchange relatively quickly with the water molecules at the surface. A straightforward, simple method is to assign a bulk relaxation time $T_{2,b}$ to the molecules distant from the surface and a relaxation time $T_{2,s}$ to the molecules at the surface, say within a monolayer adsorbed to the surface. The average relaxation time in this two-fraction model is given by [96]

$$T_{2,AV}^{-1} = \frac{f_s}{T_{2,s}} + \frac{1 - f_s}{T_{2,b}}.$$  \hspace{1cm} (4.6)

In general $T_{2,s} < T_{2,b}$ and $f_s < 1$. The fraction $f_s$ is proportional to the specific surface area $A$ (per unit volume) of the silica surface. Further, suppose the interaction between the solid and liquid is limited to a single monolayer of liquid molecules, then the fraction $f_s$ is approximated by

$$f_s = \frac{A\lambda}{1 - \phi_m},$$ \hspace{1cm} (4.7)

where $\lambda$ is the thickness of the monolayer and $\phi_m$ is the volume fraction of the solid silica content in the gel.
Table 4.1: Chemicals used for the heavy-water buffers.

<table>
<thead>
<tr>
<th>buffer</th>
<th>pH</th>
<th>composition per liter D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>2.95</td>
<td>citric acid 8.47 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaOH 3.22 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCl 2.18 g</td>
</tr>
<tr>
<td>intermediate</td>
<td>5.50</td>
<td>citric acid 12.53 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaOH 6.32 g</td>
</tr>
<tr>
<td>alkaline</td>
<td>9.48</td>
<td>di-sodiumtetraborat 3.81 g</td>
</tr>
</tbody>
</table>

Due to the hydrolysis reaction methanol is formed which is mixed with the water. In mixtures of methanol and water the molecular reorientation time of the water molecules is a function of the methanol concentration. With respect to pure water the reorientation time in solutions of methanol can increase up to 100% with increasing methanol concentration [97, 98]. Therefore, $T_{2,b}$ is a function of the methanol concentration $n_m$ in the gelling solution:

$$T_{2,b} = g(n_m, T),$$

where $g$ is an empirical function that can be determined by calibration.

4.3 Experimental section

4.3.1 Materials

Tetra-methyl-ortho-silicate, Si(OCH$_3$)$_4$, was obtained from Aldrich (>99% pure). It was dissolved in Isopar V, a mineral oil with a viscosity of about 10 mPa s at room temperature, obtained from ExxonMobil. For the aqueous phase we used D$_2$O (CIL, Andover, MA, 99.9% pure). Methanol (Merck, 99% pure) was mixed with heavy water for calibration measurements of $T_2$. Untreated D$_2$O was used for the calibration mixtures. For the bulk experiments three different buffers were prepared to control the pH by adding salts and chemicals containing normal hydrogen (see Table 4.1). The pH was measured with a semiconductor type pH meter. Pure D$_2$O was used as well in the experiments. It is noted that due to dissolution of small amounts of CO$_2$ (from the atmosphere) the untreated D$_2$O is a little acidic with a pH around 5.5. However, the buffering capacity is low, and therefore we refer to the untreated D$_2$O as unbuffered D$_2$O. Calibration gel samples were prepared by mixing TMOS with each buffer in various volume fractions $\phi_T$. The gel samples were aged at room temperature for 20 days. All gelling solutions turned into a macroscopic gel, i.e. the cross-linking gel particles percolated the entire volume of the samples, except for the gelling solution prepared with a TMOS concentration of $\phi_T^0 = 0.10$ in the pH = 9.48 buffer, which remained liquid even after 20 days of aging. All gels were transparent, but the gels prepared with the pH = 5.50 buffer were partly turbid. The two-phase bulk experiments were performed using cylindrical Teflon vials with an inner diameter of 18 mm. In each experiment 2.5 ml of water and 2.5 ml of TMOS/oil were placed in the vial. The initial volume fraction of TMOS, $\phi_T(0)$, was 0.20 or 0.35.
4.3.2 NMR measurements

Relaxation times for $^1$H and $^2$H in the samples were measured with a 0.95 Tesla NMR scanner (home-built) operating at a frequency of 40.5 MHz for hydrogen and 6.21 MHz for deuterium. The setup consists of an electro-magnet with a vertical, narrow-bore insert with an inner diameter of 31 mm. The insert is capable of producing a static magnetic gradient up to 0.2 T/m in the vertical direction. A single rf coil is used with two different front-end rf circuits for $^1$H, respectively $^2$H. Switching between the two circuits takes less than a second, allowing for a fast sequential NMR measurement of hydrogen and deuterium. A polyvinylchloride (PVC) sample holder was constructed in which a fluorocarbon fluid (Galden™ HT135, manufactured by Solvay Solexis) was circulated in order to control the temperature of the sample. The fluid is invisible to the NMR set-up and the temperature can be controlled between 10 and 65 °C with an accuracy of about 1 degree.

Details about the sequences can be found in a previous work [88]. To summarize, the $T_1$ of the hydrogen content in the oleic phase is measured to determine the TMOS concentration in oil, and the $T_2$ of the aqueous phase is measured to monitor the progress of gelation. In this case $T_2$ is measured for the deuterium content. Here a 1D static magnetic gradient is used. Since in previous measurements [88] the phases showed no significant spatial profiles in $T_1$ or $T_2$ it was decided to measure a single slice in the oleic phase and a single slice in the aqueous phase, in order to limit the total acquisition time. The measurements were repeated for each sample over an interval of 20 to 40 hours.

4.4 Results and discussion

4.4.1 Calibration experiments

Methanol-D$_2$O calibrations

The results of the relaxation time measurements are shown in Figure 4.3. At 25 °C the $T_2$ for D$_2$O is 0.389 s and decreases with increasing molar ratio of methanol, $x_M$, to 0.186 s when $x_M = 0.511$. At 50 °C the $T_2$ for D$_2$O is 0.647 s and decreases with increasing molar ratio of methanol, $x_M$, to 0.319 s when $x_M = 0.642$. The effect of mixing methanol with D$_2$O on the observed $T_2$ of the water molecules appears to be less pronounced than in case of H$_2$O [88], but agrees well with other studies on methanol-water mixtures [97, 98].

Calibration gel samples

The transverse relaxation time $T_2$ of deuterium was measured in the gels at 25 °C and 50 °C, respectively. The results are listed in Table 4.2. It is noted that the $T_2$ was not measured for the buffers without TMOS (i.e. $\phi_T^g = 0$) at 25 °C, but only for pure D$_2$O, since at 50 °C the $T_2$ appeared to be insensitive to the presence of the buffer chemicals. In all cases the relaxation time $T_2$ decreases with increasing initial TMOS concentration $\phi_T^g$. The reciprocal relaxation times are shown for the pH = 2.95 gels in Figure 4.4. The relaxation times for deuterium in the gels were fitted with Eq. 4.6 using Eq. 4.7 to
4.4. Results and discussion

Fig. 4.3: $T_2$ of the $^2$H content in the methanol-D$_2$O calibration mixtures. $x_m$ is the mole fraction of methanol. The temperature is indicated in the legend.

Table 4.2: Transverse relaxation time $T_2$ of deuterium in aqueous buffers and of deuterium in calibration gel samples. $\phi_T^g$ is the initial volume fraction of TMOS mixed with water to prepare the gels.

<table>
<thead>
<tr>
<th>$\phi_T^g$</th>
<th>no buffer</th>
<th>pH = 2.95</th>
<th>pH = 5.50</th>
<th>pH = 9.48</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C 50 °C</td>
<td>25 °C 50 °C</td>
<td>25 °C 50 °C</td>
<td>25 °C 50 °C</td>
</tr>
<tr>
<td>0.00</td>
<td>0.389 0.647</td>
<td>- 0.652</td>
<td>- 0.642</td>
<td>- 0.652</td>
</tr>
<tr>
<td>0.10</td>
<td>0.123 0.073</td>
<td>0.060 0.048</td>
<td>0.028 0.025</td>
<td>0.047 0.077</td>
</tr>
<tr>
<td>0.20</td>
<td>0.066 0.037</td>
<td>0.029 0.018</td>
<td>0.021 0.018</td>
<td>0.013 0.017</td>
</tr>
<tr>
<td>0.30</td>
<td>0.053 0.030</td>
<td>0.025 0.014</td>
<td>0.018 0.015</td>
<td>0.0084 0.0081</td>
</tr>
<tr>
<td>0.40</td>
<td>0.038 0.026</td>
<td>0.019 0.011</td>
<td>0.016 0.013</td>
<td>0.0077 0.0057</td>
</tr>
</tbody>
</table>
The effect of pH on mass transfer and gelation

4. The effect of pH on mass transfer and gelation

Fig. 4.4: Reciprocal transverse relaxation time (relaxivity) of deuterium in the acid-catalyzed gels (pH = 2.95). The solid curves indicate the obtained fits using Eq. 4.6 and the approximation for \( f_s \).

estimate \( f_s \). Furthermore, the approximation \( \phi_m = 0.2\phi_T^g \) was used, which is based on full hydrolysis and condensation of the initial TMOS content. Typical experimental values of the surface area of aero-gels, with which the dilute wet gels are compared, are on the order of 1000 \( \text{m}^2 \text{g}^{-1} \) [99], so we choose \( A = 1000 \text{m}^2 \text{g}^{-1} \) for the calculation of \( f_s \). The monolayer thickness \( \lambda \) equals 1.5 Å. The bulk relaxation time \( T_{2,b} \) of the water-methanol mixture in the pores, which is a function of \( \phi_T^g \), is derived from the calibration results of the water-methanol mixtures together with the calculation of the final water-methanol ratio in the gels. The resulting fits for the acid-catalyzed gels are shown in Figure 4.4. It can be observed that the reciprocal relaxation times increase roughly linearly with \( \phi_T^g \). The obtained surface relaxation times \( T_{2,s} \) are listed in Table 4.3. The transverse relaxation times \( T_{2,s} \) are on the order of 0.1 to 1 ms. The estimated fraction \( f_s \) varied between 0.0067 and 0.028.

4.4.2 Two-phase bulk experiments

Concentration profiles

The average TMOS concentration in the oleic phase in the two-phase bulk experiments was determined by measuring \( T_1 \) of the oleic phase [88]. For this purpose calibrations of \( T_1 \) for TMOS/Isopar V mixtures were made (see Figure 4.5), which clearly showed a monotonic increase of \( T_1 \) with increasing TMOS concentration and temperature within the temperature range considered (15–55 °C). From the derived volume fraction of TMOS in oil the number of TMOS molecules \( n_o \) in the oleic phase was calculated. The results of four bulk experiments, done at 25 °C with varying pH of the aqueous phase and with an
4.4. Results and discussion

Table 4.3: Results of the least-square fit on the relaxation time data (for deuterium) of the calibration gels using Eq. 4.6 and the approximation for $f_s$. The surface relaxation terms, $T_{2,s}$, are given for each series at both temperatures.

<table>
<thead>
<tr>
<th>pH</th>
<th>$T$ [°C]</th>
<th>$T_{2,s}$ [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>no buffer</td>
<td>25</td>
<td>1.33 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.70 ± 0.06</td>
</tr>
<tr>
<td>2.95</td>
<td>25</td>
<td>0.57 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.31 ± 0.01</td>
</tr>
<tr>
<td>5.50</td>
<td>25</td>
<td>0.41 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.33 ± 0.04</td>
</tr>
<tr>
<td>9.48</td>
<td>25</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.18 ± 0.02</td>
</tr>
</tbody>
</table>

Fig. 4.5: Average relaxation time $T_1$ of hydrogen in TMOS/Isopar V (oil) mixtures as a function of temperature. The concentration of TMOS is indicated in the legend.
4. The effect of pH on mass transfer and gelation

Fig. 4.6: Concentration of TMOS in the oleic phase as a function of time. The temperature was controlled to 25 °C. The type of buffer used is indicated in the legend. The solid curves are the fitted concentration profiles using the optimization described in Section 4.2.

initial volume fraction $\phi_T(0)$ equal to 0.35, are shown in Figure 4.6. For the pH = 9.48 case, initially, the number of molecules $n_o$ is close to the initial number ($n_o(0) = 5.88$ mmol) after which it drops gradually to almost zero within 15 hours. The unbuffered system shows a similar but faster decay, and the concentration is almost zero within 5 hours. The lower pH system (pH = 2.95) shows the fastest decay, and the mass transfer is complete within 2 hours. The lowest mass transfer rate was observed in the intermediate pH system (pH = 5.50). The mass transfer is complete only after 40 hours. Test experiments in transparent vials revealed that a weak and turbid gel was formed quickly within 2 hours in the intermediate pH systems, despite the limited transfer of TMOS within the initial 2 hours. Still, the TMOS transfers completely to the aqueous phase, and the gel does not appear to form an impermeable barrier.

The concentration profiles of all bulk experiments were fitted by optimizing the solution of Eq. 4.5, modified to include an additional offset, and show a good fit, except at small times. Due to the instant partitioning in the model the fitted profiles tend to start below the real initial concentration. From the fits the hydrolysis rate $k$ and the interaction parameter $\varepsilon_0$ were derived, all of which are listed in Table 4.4. Ideally, the derived hydrolysis rate $k$ and interaction parameter $\varepsilon_0$ should be independent of the initial concentration of TMOS used in the experiment. For most of the experiments the values agree within a factor of 2 with respect to $\phi_T(0) = 0.20$, respectively $\phi_T(0) = 0.35$. The results for the pH = 2.95 system show a bigger discrepancy. Nevertheless, considering the simplicity of the model, the results are satisfactory and reveal qualitatively the effect of pH on the hydrolysis rate, which in turn drives the mass transfer. The hydrolysis rate $k$ is on the order of $10^{-5}$ to $10^{-3}$ s$^{-1}$. Increasing the temperature always resulted in an
increased value for $k$, which is expected. The magnitude of the increase, however, varies among the systems, i.e. the factor is between 1.6 and 13. The strongest dependence of $k$ on temperature is found in the high pH system. The lowest values for $k$ are found when the pH is equal to 5.50, which is close to neutral conditions. Both the lower and higher pH system show a higher hydrolysis rate, which agrees well with literature [24, 33] (see also Figure 4.1). The pH in the unbuffered system may, due to the formation of silicic acid, slightly decrease towards 4, as was indicated by test measurements. Hydrolysis is promoted under acid-catalyzed conditions as the alkoxide groups are more easily protonated and attacked by water. Under base-catalyzed conditions the abundant hydroxyl anions attack the silicon atoms [24].

### Relaxation in the aqueous phase

For the same systems the transverse relaxation time $T_2$ of the $^2$H content in the aqueous phase was measured. The results are shown in Figure 4.7 for $T = 25 ^\circ C$ and $\phi_T(0) = 0.35$. The echo trains from which the $T_2$ was derived all showed a mono-exponential decay at all times. In addition, the subsequent $T_2$ versus time profiles are smooth and exhibit almost no scatter. In the systems at $T = 25 ^\circ C$, $T_2$ is initially about 350 ms (similar to the bulk value of D$_2$O) and decreases gradually to values below 200 ms within several hours. However, the profiles show a significant difference. In the pH = 9.48 system the $T_2$ decreases relatively quickly to 40 ms within the first 1.5 hours, after which it decreases slowly and monotonically to 9 ms during the remainder of the experiment (up to $t =
Fig. 4.7: $T_2$ of the $^2\text{H}$ content in the aqueous phase as a function of time. The measurements were done at 25 °C using four different D$_2$O solutions. The initial concentration $\phi_T(0)$ was 0.35.

47 hours). A stabilization of $T_2$ or plateau is observed after 6 hours. In the pH = 2.95 system the $T_2$ decreases quickly from 345 ms to 180 ms in the first hour, after which it decreases more slowly to 21 ms in the remainder of the experiment (up to $t = 47$ hours). The $T_2$ in the unbuffered system starts at 365 ms and decays to 50 ms in the first 6 hours of the experiment. In the pH = 5.50 system the $T_2$ decreases most rapidly and reaches a plateau at $T_2 = 24$ ms after 1.5 hours. The decay of $T_2$ is due to the cross-linking of the silica, which indicates that the condensation rate is low for the pH = 2.95 system compared to the other systems. The condensation rate appears to be the highest for the pH = 5.50 system, which corresponds to the fast gel formation observed in the transparent vials. Test measurements with the transparent vials also revealed that the gel formed in the pH = 9.48 system with $\phi_T(0) = 0.20$ did not percolate in the entire volume of the aqueous phase, and remained liquid-like. Despite complete transfer of TMOS and the fast condensation in the higher pH system the lack of percolation suggests that the silicic acid initially condenses into larger aggregates compared to the lower pH systems, in agreement with the literature [24]. As a result the formed clusters consist of colloidal particles rather than a highly branched network.

In the systems at $T = 50$ °C, $T_2$ is initially about 630 ms in the unbuffered system and drops to 58 ms within two hours. The $T_2$ in the buffered systems is initially shorter, around 540 ms, which is due to the already significant degree of hydrolysis in the initial minutes of the experiment. In the lower pH system $T_2$ drops to 20 ms within 5 hours. Both in the unbuffered system as in the pH = 2.95 system the decay of $T_2$ is faster with respect to the same systems at $T = 25$ °C, which implies that the condensation rate is higher at $T = 50$ °C. In the higher pH system with $\phi_T(0) = 0.20$, where the gel did not percolate, the decay of $T_2$ is equally fast in the initial two hours for both temperatures.
However, the final value of $T_2$ is much higher at $T = 50 \, ^\circ\text{C}$, which indicates that the relaxation behavior is similar to that of a normal liquid. Although the calibration gels were aged for 20 days, the final values of $T_2$ in the bulk experiments agree well with those of the calibration gels, and show a similar dependence of $T_2$ on $\text{pH}$ and temperature.

It was found in a previous work [88] that a minimum (plateau) in $T_2$, for $^1\text{H}$ in H$_2$O in that case, corresponded with macroscopic gelation of the aqueous phase as determined by tilting test tube experiments [88]. Similar experiments using systems of equivalent dimensions were done here at 35 °C to confirm the relation between the gel transition and the minimum (plateau) in $T_2$ for $^2\text{H}$. Again, a good agreement was found and therefore the point at which the minimum or plateau in $T_2$ is found is used to derive the gel time. The results are listed in Table 4.4. The gel time varies between 0.5 and 30 hours. The shortest gel times are found for the $\text{pH} = 5.50$ system followed by the unbuffered system and the $\text{pH} = 9.48$ system. The longest gel times are found for the $\text{pH} = 2.95$ system. Slow condensation rates are expected when the $\text{pH}$ is close to 2.5, which corresponds to the isoelectric point of silica [24, 33]. The gel time decreases roughly by a factor two when $\phi_T(0) = 0.35$ compared to the case when $\phi_T(0) = 0.20$. Increasing the temperature from 25 to 50 °C results in a reduction of the gel time of at least 50%. The effect of $\text{pH}$ on the reaction rates was only determined for a limited set of buffers (chemicals). Preparing the buffers with other chemicals or concentrations is likely to quantitatively influence the results [33].

### 4.5 Conclusion

The mechanisms of coupled mass transfer and gel reaction of TMOS in the two phase systems were revealed using a combined $^1\text{H}$ and $^2\text{H}$ NMR technique. The $\text{pH}$ of the aqueous phase is the main parameter that affects the mass transfer and the gelation rates. The mass transfer of TMOS is driven by the rate of hydrolysis. Around $\text{pH} = 6$ the rate is minimum, whereas the hydrolysis rates, and thus the mass transfer rates, are increased in the acid- and base-catalyzed systems (due to enhanced protonation of TMOS under acid conditions, respectively, enhanced attack by hydroxyl anions under alkaline conditions). At a temperature of 50 °C the rates are increased by a factor between 1.6 and 13 with respect to a temperature of 25 °C, depending on the $\text{pH}$ used. The $T_2$ of the calibration gels decreases with increasing initial TMOS content in the gelling solutions. The differences in $T_2$ for a given concentration among the various series, prepared with the different buffers, can be explained by the $\text{pH}$, which influences the microscopic structure of the silica gel. The gel transition times, derived from the $T_2$ versus time profiles revealed that the gelation rates were the highest for the $\text{pH} = 5.50$ systems (gel time on the order of 1 hour), and the lowest for the $\text{pH} = 2.95$ systems (gel time up to 30 hours). Slow condensation rates are expected when the $\text{pH}$ is close to 2.5, which corresponds to the isoelectric point of silica. Increasing the temperature from 25 to 50 °C results in a reduction of the gel time of at least 50%.
4. The effect of pH on mass transfer and gelation
Chapter 5

Cross-linking of silica with a time-dependent monomer source

In this chapter the cross-linking of the hydrolyzed TMOS molecules is considered and described using a simple population balance model. The mass transfer of the molecules from the oleic to the aqueous phase and the hydrolysis step were included in the form of a time-dependent monomer source. Gel transition times were predicted based on the critical behavior of the weight-average molecular weight of the species. Average structural properties of the silica aggregates in the gelling stage were derived. The results were used to predict the transverse relaxation time $T_2$ of the aqueous phase, which is typically measured in the NMR experiments.

5.1 Introduction

In sol-gel processing a solution of reactive monomers or colloids changes into a gel due to aggregation of the particles into larger clusters and networks. Macroscopically, the sol-gel transition occurs when the network percolates to span the entire volume of the system [100]. This transition is generally manifested by a sharp change in rheological properties, i.e. the bulk viscosity increases over several orders of magnitude [101, 102].

The aggregation of particles into clusters and fractal structures has been studied and described extensively [24]. Numerical models typically comprise the simulation of trajectories and aggregation of diffusing particles in two or three dimensions. In diffusion limited cluster-cluster aggregation models (DLCCA) the particles or clusters combine directly upon contact [103, 104]. Reaction limited cluster-cluster aggregation models (RLCCA) are similar, except that the particles only combine with a finite probability [103]. The fluctuating bond aggregation (FBA) model, which is an extension to the DLCCA model, incorporates the flexibility of the formed clusters [105]. The flexibility depends on the type of catalyst present in the sol-gel [106]. The numerical models mentioned typically yield the fractal dimension, the correlation lengths, percolation time, etc.

Population balance models describe the evolution of a molecular-weight distribution that characterizes a system of cross-linking particles. For a discrete distribution the evolution of the number of each species with a particular weight can be calculated using a kinetic equation such as the Smoluchowski equation [107, 108]. Li and McCoy proposed an elaborate model for the cross-linking of reactive species which includes the degree of cross-linking in addition to the molecular-weight balance [109].

In this chapter the aim is to describe the aggregation of hydrolyzed TMOS monomers and the evolution of the aggregates and clusters in the aqueous phase as the precursor
monomers are transferred from the oleic to the aqueous phase. We develop an algebraic model based on a population balance of polymeric species \([110, 111]\). The mass transfer of the molecules from the oleic to the aqueous phase and the hydrolysis step are included in the form of a time-dependent monomer source. A concise set of equations is obtained that can be solved analytically only for a limited set of parameters, but in many cases needs to be solved numerically. The evolution in the population balance is used to predict certain characteristics of the gelling solution, like effective surface area, and cluster mobility. In addition, the gel transition times are obtained for a set of representative systems. Finally, the transverse relaxation time \(T_2\) of the water molecules present in the gel, which is typically measured in experiments involving NMR (see Chapter 4), is considered. A simple model is proposed to predict the average transverse relaxation time \(T_2\) of the deuterium nuclei of the water molecules due to their interaction with the gelling silica content. The average \(T_2\) decays in time due to the increasing silica content and increasing cluster size. The effect of pH and temperature on the reaction rates, and hence on the \(T_2\) profiles, was modeled. The results agree qualitatively with previously obtained experimental results.

5.2 Theory

5.2.1 Mass transfer and hydrolysis

We consider again a volume consisting of two liquid phases which are in contact but separated by an interface (see also Section 3.2.1). Phase 1 initially consists of (heavy) water, and phase 2 consists of a solution of TMOS in oil with an initial concentration \(n_t(0) = n_0\). The system is shown in Figure 3.1. As the phases are put together the TMOS partitions into the aqueous phase in which it undergoes a heterogeneous sol-gel reaction. The overall mass transfer is governed by the hydrolysis rate in the aqueous phase. Each phase is well-mixed and diffusion or convection processes do not limit the mass transfer.

The total number of TMOS molecules \(n_t\) in the system decreases in the course of time due to the hydrolysis reaction. The change is described by the following kinetic equation

\[
\frac{dn_t}{dt} = \frac{d(n_o + n_w)}{dt} = -kn_w, \tag{5.1}
\]

where \(n_o\) and \(n_w\) are the number of TMOS molecules in the oleic, respectively, the aqueous phase and \(k\) is the rate of hydrolysis (where we assume full hydrolysis of the TMOS molecules). The methanol concentration \(n_m\) increases in the course of time as given by

\[
n_m(t) = 4 \int_0^t kn_w(\tau)d\tau = 4 [n_t(0) - n_t(t)]. \tag{5.2}
\]

Here we are only concerned with the typical profiles for \(n_w\) and \(n_m\) in the aqueous phase. The TMOS concentration in oil, \(n_o\), is modeled as a simple empirical function. The experiments showed (see Chapter 2) that the concentration \(n_o(t)\) can be adequately approximated by an exponential decay function

\[
n_o(t) = n_t(0) \exp(-\alpha_T t), \tag{5.3}
\]
where $\alpha_T$ is a coefficient indicating the rate of transfer. Since the mass transfer rate is controlled by the solubility of TMOS in water, and therefore by the formation of methanol in water, the coefficient $\alpha_T$ should increase with increasing $k$ and vice versa. From Eqs. 5.1, 5.2 and 5.3 it follows that

$$n_w(t) = n_t(0) \frac{\alpha_T}{k - \alpha_T} \left[ \exp(-\alpha_T t) - \exp(-kt) \right], \quad (5.4)$$

$$n_m(t) = 4n_t(0) \left\{ 1 - \frac{\alpha_T}{k - \alpha_T} \left[ \left(1 + \frac{k - \alpha_T}{\alpha_T}\right) \exp(-\alpha_T t) - \exp(-kt) \right] \right\}. \quad (5.5)$$

It is noted that Eqs. 5.4 and 5.5 do not diverge when $\alpha_T = k$. For any nonzero $\alpha_T$ and $k$ the profile of $n_w(t)$ resembles that of a distorted bell-shaped curve, and $n_m$ is a monotonically increasing function of $t$. In the following the formed amount of silicic acid due to hydrolysis is represented by $n_s$. The consumption of silicic acid due to condensation is not reflected in $n_s$, so that

$$n_s(t) = 4n_m(t). \quad (5.6)$$

### 5.2.2 Population balance model

#### General equations

Let $P(x)$ denote a continuous distribution of molecules with weight $x$ at a certain instant. In case of irreversible aggregation the reaction between two aggregates or larger clusters (see Figure 5.1) is represented by

$$P(x) + P(x') \xrightarrow{k_p} P(x + x'), \quad (5.7)$$

where the reaction rate $k_p$ should be an increasing function of the molecular sizes or weights. A general rate kernel is defined as [111]

$$k_p(x, x') = \kappa(x x')^\nu, \quad (5.8)$$

where $\kappa$ is a constant and $\nu$ is a value between 0 and 1. Next, let $p(x, t)dx$ be the concentration of molecules at time $t$ with molecular weight in the range $(x, x + dx)$. The population balance equation can be written as (based on Ref. [111])

$$\frac{\partial p(x, t)}{\partial t} = -2\kappa x^\nu p(x)p^{[\nu]} + \kappa \int_0^x (x')^\nu(x - x')^\nu p(x - x')p(x')dx' + S, \quad (5.9)$$

where the bulk moment $p^{[\nu]}$ is defined as

$$p^{[\nu]} = \int_0^\infty x^np(x)dx, \quad (5.10)$$

and the source term $S$ is due to the hydrolysis of TMOS into silicic acid monomers, given by

$$S = kn_w(t)\delta(x - x_m), \quad (5.11)$$
where $x_m$ is the molecular weight of the monomer. Application of Eq. 5.10 to Eq. 5.9 yields a coupled set of ordinary differential equations (ODEs) for the bulk moments. In order to extract the number and weight average molecular weights of the population it suffices to consider the moments of order $n = 0, 1, 2$. The ODEs are given by

\[ \frac{dp^{[0]}}{dt} = -\kappa (p^{[\nu]})^2 + kn_w, \] (5.12)

\[ \frac{dp^{[1]}}{dt} = kn_w x_m, \] (5.13)

\[ \frac{dp^{[2]}}{dt} = 2\kappa (p^{[1+\nu]})^2 + kn_w x_m^2. \] (5.14)

The initial conditions are given by

\[ p^{[n]}(0) = 0, \quad n = 0, 1, 2. \] (5.15)

In general, equations 5.12 through 5.15 need to be solved numerically. For any $\nu$ not equal to 0 or 1 the set of equations needs to be solved using closure conditions to account for the fractional moments. The non-integer moments $p^{[\nu]}$ and $p^{[1+\nu]}$ are determined from the integer moments by using an interpolation method [112]. The reduced moment $\tilde{p}^{[\nu]} = p^{[\nu]} / p^{[0]}$ is obtained through a Lagrange interpolation of the available integer moments (up to order $N$), i.e.

\[ \log \tilde{p}^{[\nu]} = \mathcal{L} \left( \log \tilde{p}^{[0]}, \log \tilde{p}^{[1]}, ..., \log \tilde{p}^{[N]} \right), \] (5.16)

where the operator $\mathcal{L}$ represents the Lagrange interpolation. In order to obtain an accurate interpolation, the original second-order scheme (Eqs. 5.12 - 5.14) is extended to a fourth-order scheme by including the equations

\[ \frac{dp^{[3]}}{dt} = 6\kappa p^{[1+\nu]} p^{[2+\nu]} + kn_w x_m^3, \] (5.17)

\[ \frac{dp^{[4]}}{dt} = \kappa \left\{ 8p^{[1+\nu]} p^{[3+\nu]} + 6 (p^{[2+\nu]})^2 \right\} + kn_w x_m^4. \] (5.18)
5.2 Theory

Derivative parameters of moments

The distribution of the aggregates can be characterized by the number-average molecular weight \( M_n \), equal to \( p^{[1]}/p^{[0]} \), and by the weight-average molecular weight \( M_w \), equal to \( p^{[2]}/p^{[1]} \) [111]. The gel transition of the system can, from a mathematical point of view, be linked to the divergence of the second and higher order moments, which occurs at a transition time \( t_c \) when \( \nu \) is greater than a critical value \( \nu_c \). Likewise, \( M_w \) will diverge at such a transition, which, for a batch system containing a fixed initial amount of aggregating monomers, is often represented by the power law [111]

\[
\tilde{M}_w(t) = \tilde{M}_w(0) \left(1 - \frac{t}{t_c}\right)^{-\gamma},
\]

(5.19)

where the critical parameters are the gel time \( t_c \) and the exponent \( \gamma \).

5.2.3 Gelation and percolation

Structural evolution of aggregates

The population balance model yields the number- and weight-average molecular weight as a function of time, but does not predict the structural evolution of the aggregates. The growth mechanisms are complex and depend strongly on the type of catalyst and the water/TMOS ratio [33, 99]. Furthermore, after gelation the internal structure changes due to dissolution and secondary cross-linking of the silica, which is referred to as aging [24]. A rigorous description of the mechanisms is out of the scope, and a phenomenological approach is employed instead.

In the early stage of the condensation process the monomers and small oligomers combine into compact, spherical aggregates with a characteristic size \( R_A \) and weight \( x_A \). The weight \( x_A \) follows from

\[
\frac{x_A}{x_m} = \left(\frac{R_A}{a}\right)^3,
\]

(5.20)

where \( a \) is the size of a monomer. Subsequently, in the intermediate stage the non-fractal aggregates interlink to form fractal clusters with a fractal dimension \( d_f \) [113, 114]. Eventually, the clusters start to link into larger networks. On the scale of the network the fractal character is lost [115]. Gelation occurs when all clusters combine into a single network. Percolation, i.e. macroscopic gelation, occurs when the network spans the entire volume of the system. The size \( R_A \) ranges from several nanometers (at low pH) to several microns (at high pH) [34], which is shown schematically in Figure 5.2. The growth of the large compact aggregates under base-catalyzed conditions is promoted since nucleation and growth is the dominant growth mechanism, which is facilitated by the enhanced depolymerization rate [33] (see also Figure 5.3).

In the intermediate stage the effective cluster radius \( R_{\text{eff}} \) is related to the average molecular weight through

\[
R_{\text{eff}} \approx R_A \left(\frac{\tilde{M}_w}{x_A}\right)^{1/d_f}.
\]

(5.21)
5. Cross-linking of silica with a time-dependent monomer source

Fig. 5.2: Polymerization behavior of aqueous silica. In basic solution (B) particles grow in size with a decrease in number; in acid solution or in the presence of flocculating salts (A), particles aggregate into three-dimensional networks and form gels. After Iler [34].

Fig. 5.3: Schematic representation of the pH-dependence of hydrolysis (H), condensation (C), and dissolution (D) in an alkoxy-silane solution. In this case H₂O:Si = 1.5. After Brinker [33].
As the clusters grow in time their volume fraction in the system, \( \phi \), increases relative to the volume fraction of the monomeric units, according to [115] (provided the size distribution is narrow)

\[
\phi(t) = \phi_m(t) \left( \frac{R_{\text{eff}}}{R_A} \right)^{(3-d_f)} = \phi_m(t) \left( \frac{\bar{M}_w}{x_A} \right)^{(3-d_f)/d_f},
\]

where \( \phi_m \) is the volume fraction of the monomeric units, given by

\[
\phi_m(t) \approx \frac{4}{3} \pi a^3 n_s(t) V(t)^{-1}.
\]

The volume \( V \) in Eq. 5.23 increases due to the transfer of TMOS, and is given by

\[
V(t) = V_0 + [n_t(0) - n_o(t)] \bar{v}_T,
\]

where \( V_0 \) is the initial volume of the aqueous phase and \( \bar{v}_T \) is the molecular volume of TMOS. Formally, when the volume fraction \( \phi \) becomes greater than one the clusters start to overlap and will aggregate to form a percolating network that spans the entire volume.

### Internal surface of silica clusters

In case the monomers would aggregate to form solid spheroids \((d_f = 3)\) the total surface area \( A \) per unit volume \([\text{m}^{-1}]\) is

\[
A \approx \frac{\phi_m}{3 R_{\text{eff}}}. \tag{5.25}
\]

The situation becomes more complicated when the aggregates or clusters are fractal. The magnitude of accessible surface area is also dependent on the scale at which the fractal structure is considered. An extreme case, at low concentrations, is where the network consists of weakly cross-linked chains of a monomer thick. The surface area is then approximated by

\[
A \approx \frac{3 \phi_m}{a}. \tag{5.26}
\]

Equation 5.25 yields the lowest possible surface area for a given \( \phi_m \), whereas Eq. 5.26 gives the highest possible magnitude.

### Mobility of aggregates

For small aggregates and clusters the mobility can be related to their sizes. With the condition that the shapes of the aggregates are spherical the rotational diffusion coefficient \( D_R \) is approximated by

\[
D_R = \frac{k_B T}{4 \pi \eta R_{\text{eff}}^3}. \tag{5.27}
\]

For larger clusters and in case of percolation the rotational mobilities will obviously be close to zero due to steric effects.
5.2.4 Nuclear magnetic relaxation of deuterium in gel

The discussion of the relaxation of deuterium is focussed on the $T_2$ of the D$_2$O molecules in the gelling solutions. The transverse relaxation time $T_2$ is given by [41]

$$\frac{1}{T_2} = \frac{1}{160} \left( 1 + \frac{\eta^2_A}{3} \right) Q_{cc}^2 \{ 9 J(0) + 15 J(\omega_0) + 6 J(2\omega_0) \}, \quad (5.28)$$

where $\eta_A$ is an asymmetry parameter (close to zero), $Q_{cc}$ is the quadrupolar coupling coefficient (about $1.38 \times 10^6$ rad s$^{-1}$) and $\omega_0$ is the Larmor frequency. The function $J$ in Eq. 5.28 describes the effect of molecular fluctuations on the relaxation times at a given resonance frequency. The only molecular fluctuation of importance is the molecular rotation. When the rotational motion is assumed to be random and characterized by a typical ”tumbling” or correlation time $\tau_c$ then a Lorentzian function is used for $J$, given by

$$J(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2}. \quad (5.29)$$

Eq. 5.29 reduces to $J = 2\tau_c$ in the so-called fast motion limit, where $\omega_0^2\tau_c^2 \ll 1$.

As the water molecules diffuse through the system they adsorb onto or interact with the growing silica clusters, with a finite probability. An important interaction mechanism between the water and the silica is due to hydrogen (deuterium) bonding with the abundant silanol groups.

From a macroscopic point of view, the relaxation behavior can be modeled by assigning different phases in which a nucleus resides during a certain life time [94, 96, 116]. Each phase $i$ corresponds to a relaxation time $T_{2,i}$ brought about by an effective correlation time $\tau_{ci}$. In the sol-gel the silica is dispersed on the scale of nanometers. Therefore the average relaxation is described by a fast-exchange model. A bulk relaxation time $T_{2,b}$ is defined for the molecules distant from the surface and a surface relaxation time $T_{2,s}$ is defined for the molecules near the surface. The average relaxation time in this two-fraction model is given by [96]

$$T_{2,AV}^{-1} = \frac{f_s}{T_{2,s}} + \frac{1 - f_s}{T_{2,b}}, \quad (5.30)$$

where $f_s$ is the fraction of nuclei in the surface phase. In general $T_{2,s} < T_{2,b}$ and $f_s < 1$. The fraction $f_s$ is proportional to the specific surface area $A$ of the silica surface. In case the interaction between solid and liquid is limited to a single monolayer of liquid molecules the fraction $f_s$ would be approximated by

$$f_s = \frac{A \lambda}{1 - \phi_m}, \quad (5.31)$$

where $\lambda$ is the thickness of the monolayer.

The molecular reorientation times of the water molecules govern the surface relaxation times $T_{2,s}$. Generally, the correlation times of the D$_2$O molecules near the surface will increase compared to those of bulk water. The relaxation time $T_{2,b}$ is a function of the methanol concentration in solution [97, 98] and is obtained from calibration.
Table 5.1: Transverse relaxation time $T_2$ of deuterium in methanol (CH$_3$OH) - D$_2$O mixtures. $x_M$ is the molar fraction of methanol, and $T$ is the temperature.

<table>
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5.3 Results and discussion

5.3.1 Experimental observations

Some results of the experimental work on the two-phase bulk systems using NMR techniques (see Chapter 4) are briefly reviewed below. This is done for two reasons. First, the profiles of $n_o$ versus time are considered in order to derive a set of coefficients for the mass transfer rate $\alpha_T$ (defined by Eq. 5.3), which are based on the experimental systems. Secondly, the obtained $T_2$ profiles are considered, since the population balance model described above is used to predict (qualitatively) the reduction of $T_2$ due to the sol-gel reaction.

Transverse relaxation in calibration fluids and gels

The effect of methanol in solution on the bulk relaxation time of D$_2$O was determined by preparing calibration mixtures containing pure methanol and pure D$_2$O. The transverse relaxation time $T_2$ was measured for deuterium at a temperature of 25 $^\circ$C and 50 $^\circ$C, respectively. The results are given in Table 5.1.

Calibration gels were prepared from gelling solutions of TMOS in heavy water with or without buffer. The initial concentration of TMOS, $\phi_T^0$, was varied between 0.10 and 0.40. The gels were aged for 20 days. The transverse relaxation time $T_2$, which was measured at 25 $^\circ$C and 50 $^\circ$C, were found to decrease with increasing $\phi_T^0$.

It was found that the relaxation times could adequately be described by Eq. 5.30. The bulk relaxation time $T_{2,b}$ of the water/methanol mixture in the pores, which is a function of $\phi_T^0$, was derived from the calibration results of the water/methanol mixtures together with the calculation of the final water/methanol ratio in the gels. The fraction $f_s$ was approximated by Eq. 5.31.
Two-phase bulk experiments

The number of TMOS molecules $n_o$ in the oleic phase versus time for three bulk experiments, done at 25 °C with varying pH of the aqueous phase, are shown in Figure 5.4. All concentration profiles were fitted with Eq. 5.3, modified to include an additional offset (to account for noise present in the profiles), yielding an excellent description of the data. From the fits the mass transfer rate coefficients $\alpha_T$ were derived, which are listed in Table 5.2.

The transverse relaxation time ($T_2$) profiles of $^2$H in the aqueous phase are shown in Figures 5.5 and 5.6 for $T = 25$ °C and $T = 50$ °C. At $T = 25$ °C, $T_2$ is initially about 350 ms (similar to the bulk value of D$_2$O) and decreases gradually to values below 100 ms within several hours. However, the profiles show a significant difference. In the pH = 9.48 system $T_2$ decreases relatively quickly to 100 ms within the first 5 hours, after which it decreases slowly and monotonically to 30 ms during the remainder of the experiment (up to $t = 47$ hours). In the pH = 2.95 system $T_2$ decreases quickly from 335 ms to 250 ms in the first hour, after which it decreases more slowly to 34 ms in the remainder of the experiment (up to $t = 47$ hours). In the unbuffered system $T_2$ starts at 360 ms and decays to 73 ms in the first 10 hours of the experiment. In the systems at $T = 50$ °C, $T_2$ is initially about 630 ms in the unbuffered system and drops to 58 ms within two hours. In the buffered systems $T_2$ is initially shorter, around 540 ms, which is due to the already significant degree of hydrolysis in the initial minutes of the experiment. In the lower pH system $T_2$ drops to 20 ms within 5 hours. Both in the unbuffered system as in the pH = 2.95 system the decay of $T_2$ is faster with respect to the same systems at $T = 25$ °C,
Table 5.2: Fitted mass transfer coefficient $\alpha_T$ for the various bulk experiments. The hydrolysis reaction rate $k$ is equal to $1.5 \times \alpha_T$. The condensation rate $\kappa$ and the colloidal size $R_A$ which are used in the model calculations are listed as well. $t_c$ is the obtained critical transition time of $\bar{M}_w$, and $t_g$ is the gel transition time at which $\phi = 1$. $t_g^{exp}$ is the experimental gelation time.

<table>
<thead>
<tr>
<th>$T$ [$^\circ$C]</th>
<th>pH</th>
<th>$\alpha_T$ [h$^{-1}$]</th>
<th>$k$ [h$^{-1}$]</th>
<th>$\kappa$ [h$^{-1}$]</th>
<th>$R_A$ [nm]</th>
<th>$t_c$ [h]</th>
<th>$t_g$ [h]</th>
<th>$t_g^{exp}$ [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>no buffer</td>
<td>0.52</td>
<td>0.78</td>
<td>100</td>
<td>10</td>
<td>7.5</td>
<td>7.4</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>25</td>
<td>2.95</td>
<td>0.86</td>
<td>1.29</td>
<td>15</td>
<td>1</td>
<td>27.5</td>
<td>27.4</td>
<td>30 ± 3</td>
</tr>
<tr>
<td>25</td>
<td>9.48</td>
<td>0.23</td>
<td>0.35</td>
<td>500</td>
<td>1000</td>
<td>5.3</td>
<td>5.2</td>
<td>n.a.</td>
</tr>
<tr>
<td>50</td>
<td>no buffer</td>
<td>0.67</td>
<td>1.01</td>
<td>700</td>
<td>20</td>
<td>2.6</td>
<td>2.5</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>50</td>
<td>2.95</td>
<td>2.22</td>
<td>3.33</td>
<td>100</td>
<td>2</td>
<td>4.8</td>
<td>4.7</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>50</td>
<td>9.48</td>
<td>1.06</td>
<td>1.60</td>
<td>1000</td>
<td>2000</td>
<td>1.7</td>
<td>1.6</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

which implies that the condensation rate is higher at $T = 50$ $^\circ$C.

The faster decay of $T_2$ in the first 10 hours for the higher pH system compared to the lower pH system is indicative of a faster condensation rate, since the extent of the TMOS transfer between the two phases is actually greater for the lower pH system and the fact that a fast mass transfer must be linked to a high hydrolysis rate. For example, at $t = 3$ hours about half of the TMOS in the pH = 9.48 system has transferred from the oleic to the aqueous phase, whereas the transfer is almost complete in the pH = 2.95 system. However, at $t = 3$ hours the $T_2$ for the latter system is 300 ms and for the higher pH system $T_2$ is 150 ms.

5.3.2 Model calculations

Population balance evolution

Model calculations were performed using the simple mass transfer and population balance model described in Section 5.2. The ODEs were solved numerically with a straightforward explicit scheme with a sufficiently small time step. With regard to the mass transfer and hydrolysis rates six sets of parameters were chosen to reflect the different pH in the six experimental systems. Since the mass transfer is promoted by a higher rate of hydrolysis, the hydrolysis rate $k$ is linked directly to the mass transfer rate $\alpha_T$. We arbitrarily choose the linear relation $k = 1.5 \times \alpha_T$. The hydrolysis reaction rate constants $k$ are given in Table 5.2 for each system.

The number of TMOS molecules in both phases $n_o$, respectively, $n_w$ as functions of time are calculated using Eqs. 5.3 and 5.4. The profiles for the base-catalyzed system are shown in Figure 5.7. Like the amount of TMOS in oil, $n_o$, the total amount of TMOS, $n_t$, decreases monotonically with time and becomes almost zero after about 20 hours. The profile of the amount of TMOS in water, $n_w$, exhibits a distorted bell shape. At $t = 0$, $n_w$ is zero and reaches a maximum after about 4 hours, after which it decreases gradually to zero. The total amount of hydrolyzed TMOS, in the form of silicic acid monomers or aggregates, is equal to the first moment $p^{[1]}$, the profiles of which are shown in Figure 5.8.
5. Cross-linking of silica with a time-dependent monomer source

**Fig. 5.5:** $T_2$ of the $^2$H content in the aqueous phase as a function of time. The measurements were done at 25 ºC using three different D$_2$O solutions. The initial concentration of TMOS in the oleic phase $\phi_T(0)$ equals 0.20.

**Fig. 5.6:** $T_2$ of the $^2$H content in the aqueous phase as a function of time. The measurements were done at 50 ºC using three different D$_2$O solutions. The initial concentration of TMOS in the oleic phase $\phi_T(0)$ equals 0.20.
5.3. Results and discussion

In all systems $p^{[1]}$ increases monotonically towards a final value equivalent to the initial amount of TMOS $n_t(0)$, but the increase for the lower pH system is faster than for the intermediate and higher pH system in the initial stage.

Several calculations were done varying the exponent $\nu$ and coefficient $\kappa$ in the reaction rate kernel $k_p$, in order to examine the cross-linking reaction in more detail. Two sets of calculations are discussed which form an illustrative example. In the first set $\kappa = 10 \, \text{h}^{-1}$ and in the second set $\kappa = 20 \, \text{h}^{-1}$. In both cases $\nu$ was varied, having the values 1/3, 2/3 or 3/4. Though several parameters were calculated we here focus on the weight-average molecular weight $\bar{M}_w$ being equal to $p^{[2]} / p^{[1]}$. The results are demonstrated in Figure 5.9.

Several aspects can be observed. First, in all cases $\bar{M}_w$ is initially equal to 1 and increases monotonically in time. Secondly, within the time interval considered, $\bar{M}_w$ does not diverge when $\kappa = 10 \, \text{h}^{-1}$, irrespective of $\nu$. However, when $\kappa = 20 \, \text{h}^{-1}$ the parameter $\bar{M}_w$ diverges for all pH systems when $\nu = 3/4$ and also for the lower pH system and unbuffered system when $\nu = 2/3$. The curve for the higher pH system with $\nu = 2/3$ is close to divergence and will do so after 30 hours. When $\nu = 1/3$, the results of which are not demonstrated here, none of the curves show critical behavior, even after extended calculation times. Other calculations were done as well with $\kappa = 50, 100, 200, 500$ and $1000 \, \text{h}^{-1}$. In general, the results show that increasing values of either $\nu$ or $\kappa$ always lead to a faster monotonous increase of $\bar{M}_w$, and likewise, a shorter transition time at which the critical behavior occurs (in case $\nu = 2/3$ or $3/4$). Due to the slower mass transfer and hydrolysis in the higher pH system the silicic acid source is weaker and therefore, given a particular combination of $\nu$ and $\kappa$, the increase (and divergence) of $\bar{M}_w$ is delayed with respect to the lower pH system.

Fig. 5.7: Predicted number of TMOS molecules in the model system at $p\text{H} = 9.48$ and $T = 25 \, ^\circ\text{C}$

Fig. 5.8: First moment of the population balance. The thick lines indicate the systems at $50 \, ^\circ\text{C}$, the thin lines indicate the systems at $25 \, ^\circ\text{C}$.
5. Cross-linking of silica with a time-dependent monomer source

Fig. 5.9: Calculated weight-average molecular weight $\bar{M}_w$ using the population balance model. The model systems representing the three pH systems at 25 °C were considered. The thick lines indicate the calculations using $\nu = 3/4$, the thin lines indicate the calculations using $\nu = 2/3$; (left) $\kappa = 10 \, \text{h}^{-1}$, (right) $\kappa = 20 \, \text{h}^{-1}$.

Fig. 5.10: Calculated critical transition time $t_c$ (indicated by the symbols) as a function of $\kappa$ or $n_0$ for each model system (see Table 5.2). In this case $\nu = 3/4$. The solid curves represent the fit using the power law in Eq. 5.32. (left) variation of $\kappa$. (right) variation of $n_0$. 
5.3. Results and discussion

Prediction of gel times

The mass transfer rate and hydrolysis coefficient given in the previous section were used again. The exponent $\nu$ was set to $3/4$, in agreement with Li and McCoy [111]. The fractal dimension $d_f$ was always 2.2 [117]. The size of the colloids in the initial stage of the condensation process, $R_A$, was varied as a function of $pH$ and temperature (see Table 5.2). The condensation coefficients $\kappa$ were varied in order to reflect the difference in gelation rates, as observed in the experiments. The critical transition time $t_c$ was obtained by fitting the profiles of $\bar{M}_w$ (not shown) with Eq. 5.19 and fixing the exponent $\gamma$ to 2.7 [111]. The resulting values for $t_c$ are shown in the left-hand graph of Figure 5.10 for each system as a function of $\kappa$. It can be observed that $t_c$ decreases with increasing $\kappa$. The calculated points in Figure 5.10 were fitted with the following power law:

$$t_c = c\kappa^{-\beta},$$

where $c$ and $\beta$ are constants. For each set the fit is adequate in the range of $\kappa$ between 20 and 1000 h$^{-1}$.

In Table 5.2 the values for $\kappa$ are listed that resulted in a satisfactory match between the experimentally obtained gelation time $t_{\text{exp}}^g$ (from the NMR experiments) and the critical transition time $t_c$. It is noted that the base-catalyzed systems in the experiments did not gel macroscopically. For these systems $\kappa$ was chosen relatively high, in order to reflect the fast condensation rate at a $pH$ around 9 (see Figure 5.3). Next, given the specified values for $\kappa$, the initial concentration of TMOS, $n_0$, was varied and the critical times $t_c$ were extracted. The results are shown in the right-hand graph of Figure 5.10. Again, the points were adequately fitted with the power law in Eq. 5.32. It is noted that for each system $\alpha_T$ and $k$ were fixed and independent of $n_0$, which is a simplification. It follows that an increase in the initial TMOS concentration by a factor 2 results in a reduction of the gel time by a factor between 1.3 and 2.1. This is consistent with the gel times obtained in the experiments (see Chapter 4).

Besides the critical behavior of $\bar{M}_w$ the critical growth of $\phi$ was considered. The time, $t_g$, at which $\phi \approx 1$ was extracted from the calculated data. Since $\phi$ increases monotonically with $\bar{M}_w$ it diverges like $\bar{M}_w$ close to $t_c$. The obtained times $t_g$ are slightly lower than $t_c$ for each system (see Table 5.2). The magnitudes of $R_A$ had a negligible effect on the transition times $t_g$. Despite the lack of macroscopic gelation (percolation) in the experimental base-catalyzed systems, the transition ($\phi > 1$) did occur in the model systems, since $\phi$ always diverged.

Prediction of $T_2$

$T_2$ was calculated for all model systems given the mass transfer rates, hydrolysis rates and condensation coefficients in Table 5.2. The volume fraction of the total hydrolyzed silica content $\phi_m$ was readily calculated using Eqs. 5.23 and 5.24. We used the upper-limit approximation of the internal surface area $A$ according to Eq. 5.26. The monomeric size $a$ is based on the density and molar weight of silica, yielding $a \approx 2.3$ Å. The fraction $f_s$ then follows from Eq. 5.31 together with the choice $\lambda = 1.5$ Å. In these calculations $f_s$ grows from zero to about 0.07. The final internal surface area would correspond to
a value of about 6700 m$^2$ g$^{-1}$, which is rather high. Typical experimental values of the surface area of aero-gels, with which the dilute wet gels are compared, are on the order of 1000 m$^2$ g$^{-1}$ [99]. Therefore, $A(t)$ is divided by a factor 6.7 to yield a more realistic surface area. The fraction $f_s$ scales accordingly. For all systems $f_s$ increases from zero to 0.0104. With the assumption that the modulation of the nuclei can be described by a single effective correlation time $\tau_s$ the average relaxation time $T_2$ was calculated using Eqs. 5.28, 5.29 and 5.30. The resonance frequency $\omega_0$ was set to $3.90 \times 10^{-7}$ rad s$^{-1}$. The bulk value $T_{2,b}$ follows from the calibration measurements of the methanol-D$_2$O mixtures, and the calculated methanol fraction.

A qualitative agreement between the model calculation and the experiments is obtained with the approximation that $\tau_s$ is inversely proportional to $D_R$. Because $D_R$ is a function of $\bar{M}_w$ it will drop to zero once $\bar{M}_w$ diverges, which occurs in the higher pH system at $t \approx 5$ hours. This would result in $\tau_s$ going to infinity. Instead a maximum value of 2 ns is imposed on the correlation time so that $T_2$ does not become shorter than 0.050 s. For the $T = 50$ °C case this is 54 ms, due to a difference in $T_{2,b}$. The profiles, calculated with the choice $\tau_s = 100 \times D_R^{-1}$, for all systems are shown in Figure 5.11. At $T = 50$ °C the decay of $T_2$ is always faster for a given pH than at $T = 25$ °C, which agrees with the experimental observations. The discontinuities in the graphs are due to the truncation of $\tau_s$ at 2 ns. A smoother truncation is required near the point where $\tau_s$ diverges, to obtain a better physical representation of $T_2$. The differences in the plateau values, observed in the experiments, could either be modeled by scaling the fraction $f_s$ or by changing the truncation value for $\tau_s$. 

**Fig. 5.11:** Calculated profiles of $T_2$ for the model systems. The correlation time $\tau_s$ equals $100 \times D_R^{-1}$ with a maximum of 2 ns. The thick lines indicate the systems at 50 °C, the thin lines indicate the systems at 25 °C.
5.4 Conclusion

The cross-linking of silica monomers, which are gradually formed through the hydrolysis of a precursor, was described with a population balance model including a time-dependent source term. This way, the effect of both the hydrolysis and the condensation rate on the population balance evolution could be modeled. Like in common population balance calculations, which usually involve a fixed initial amount of particles, the weight-average molecular weight of the aggregates grows critically and diverges at the gel transition point. However, besides the condensation rate, the hydrolysis rate, which is included in the source term, influences the gel transition time. The higher the hydrolysis and the condensation rates, the shorter is the gel time. Furthermore, increasing the initial TMOS concentration by a factor 2 results in a reduction of the gel time by a factor between 1.3 and 2.1. Finally, a qualitative agreement between the predicted profiles for $T_2$ and the experimental profiles was found using simple relations between the average aggregate mobility and the correlation time of the water molecules.
Part II

Gel placement in porous materials
Chapter 6

Coupled mass transfer and gelation of TMOS in porous materials

In the previous chapters the coupled mass transfer and gelation of TMOS in two-phase bulk models was considered. Here we turn to the situation in which TMOS, dissolved in oil, is forced into a natural porous material containing (heavy) water. The coupled mass transfer and gel reaction were characterized and monitored by employing bi-nuclear NMR techniques. The relaxation time $T_1$ of hydrogen in the oleic phase was measured to determine the mass transfer rate, and the relaxation time $T_2$ of deuterium in the aqueous phase was measured to determine the reaction rate. It was found that, like in bulk systems, the mass transfer is predominantly driven by the hydrolysis rate. Due to the gel treatment, for each core the relative permeability to water was reduced more than that to oil.

6.1 Introduction

When an alkoxy-silane solution in oil is forced into a porous material containing water the chemical transfers and reacts with water on a pore scale. Silica gel is then formed, which alters the pore space or blocks the pores. A series of experiments was done to characterize and monitor in situ the placement and reaction of TMOS in a natural porous material.

Consider a homogeneous porous cylinder (core) with a length $L$, porosity $\phi$ and absolute permeability $K_{\text{abs}}$ (see Figure 6.1). The core is fully saturated with an aqueous phase and an oleic phase. The water saturation is given by $S_w(z,t)$, where $z$ is the spatial coordinate along the length of the core. Consequently, the oil saturation $S_o(z,t)$ is equal to $1 - S_w$. The volume fraction of TMOS in the oleic phase is given by $\phi_T(z,t)$. A mixture of TMOS/oil, with a fraction $\phi_T = \phi_0$, is injected with an injection rate $Q$ at the inlet of the core, which is located at $z = -L/2$, and subsequently fluids are produced at the outlet which is located at $z = L/2$. As the TMOS comes in contact with water, the TMOS partitions between both phases. In the aqueous phase the TMOS undergoes a heterogeneous reaction with water and forms a gel.

To our best knowledge, the coupled mass transfer and gel reaction of TMOS have so far not been monitored in situ in natural porous materials. To do so, we developed and employed dedicated NMR techniques to measure the mass transfer and reaction rates of the chemical within small sandstone cores which were prepared at either irreducible water or residual oil conditions [118]. Discrimination between both phases was done by using heavy water instead of normal water for the aqueous phase and by employing both $^1$H-NMR and $^2$H-NMR techniques to measure the relaxation times of the oleic phase and the
6. Coupled mass transfer and gelation of TMOS in porous materials

**Fig. 6.1:** Model of porous system (core), having a length $L$, cross-section $A$, porosity $\varphi$ and absolute permeability $K_{abs}$. The fluids are injected at the inlet ($z = -L/2$) with a flux $Q$. In this example the water saturation ($S_w$) profile represents a drainage process. The outlet pressure at $z = L/2$ is equal to $P_{out}$.

aqueous phase, respectively. Additionally, the effect of the gel treatment on the (relative) permeability of the cores was determined by measuring the differential pressure over the cores while injecting oil, respectively water at a given flow rate. The effect of $pH$ and temperature on the reactive transport was investigated and compared to the bulk model results described in Chapter 4.

The measurement of NMR relaxation times of fluids or gels (containing hydrogen or deuterium) in porous materials is not trivial. Therefore, we briefly discuss the main properties that we need to interpret our experiments. Two aspects need to be considered; the intrinsic relaxation of the fluids or gels, and the effect of the porous material on the relaxation behavior.

First of all, within a saturated porous material the relaxation times of the fluid(s) are affected by the solid content of the porous structure. Interaction between the fluid molecules and the pore wall in general leads to enhanced relaxation rates, depending on the polarity of the fluid and the surface structure and chemistry of the pore wall. The smaller the pore, the higher is the relative number of molecules that, due to diffusion (Brownian motion), come in contact with the surface within a fixed time interval. Therefore the reduction of the average $T_1$ and $T_2$ increases with decreasing pore size [119]. The enhanced average relaxation rate of the molecules near the surface can be explained by several mechanisms. For example, when the fluid molecule adsorbs temporarily at the surface or forms hydrogen bonds with a solid molecule, the mobility is temporarily reduced and, hence, the relaxation rate is enhanced [94]. Another effect is due to the presence of paramagnetic elements in the solid which effectively increase the relaxation rates of the fluid molecules through dipolar interaction, especially with respect to elements with a large gyromagnetic ratio such as $^1H$ [120].

In case of a multi-phase system the mechanisms mentioned above are important only for the wetting phase. The third mechanism, which holds for all fluid molecules in the pores, is due to the difference in magnetic susceptibility between the fluid and the solid. Local magnetic gradients are found on the pore scale, the magnitude of which increases with increasing main magnetic field of the NMR scanner [49]. The presence of a magnetic gradient reduces the apparent relaxation time $T_2$ that is measured with the CPMG sequence. This is due to enhanced dephasing of the spins brought about by diffusion of the molecules within the magnetic gradient [121]. The reduction of $T_2$ increases with
increasing echo time, gradient strength, diffusion coefficient and gyromagnetic ratio.

In a porous material the presence of paramagnetic impurities or internal magnetic gradients has little effect on the relaxation of D\textsubscript{2}O compared to H\textsubscript{2}O. Moreover, the use of D\textsubscript{2}O instead of H\textsubscript{2}O allows for a clear separation between the oleic phase (containing \textsuperscript{1}H) and the aqueous phase. For these reasons, the use of D\textsubscript{2}O is preferred, despite the relatively weak NMR signal of deuterium [122].

As for the intrinsic relaxation of the fluids and gels, the relaxation of hydrogen in bulk mixtures, such as TMOS/oil, was discussed in Chapter 2. The relaxation of the deuterium atoms in the silica gels, prepared with D\textsubscript{2}O, is due to intra-molecular quadrupole interaction [41], and is sensitive to the mobility of the molecules. $T_2$ is shorter for the gels than for bulk D\textsubscript{2}O. In gelling solutions, $T_2$ is initially similar to that of bulk D\textsubscript{2}O, but it becomes shorter in the course of time and reaches a plateau at the gel time. The final reduction in $T_2$ increases with increasing initial TMOS content of the gelling solution. The main contribution to the reduction in $T_2$ is due to the interaction (e.g. adsorption) of the D\textsubscript{2}O molecules with the silica network.

6.2 Experimental section

6.2.1 Materials and methods

Tetra-methyl-ortho-silicate, Si(OCH\textsubscript{3})\textsubscript{4}, was obtained from Aldrich (>99% pure). It was dissolved in Isopar V, a mineral oil with a viscosity of 10 mPa s at room temperature, obtained from ExxonMobil. The volume fraction of TMOS in oil was always equal to 0.20. For the aqueous phase we used D\textsubscript{2}O (CIL, Andover, MA, 99.9% pure). In addition, three different D\textsubscript{2}O buffers were prepared by adding salts and chemicals containing normal hydrogen in little amounts. The pH was measured with a semiconductor type pH meter. The low pH buffer ($p\text{H} = 2.84$) contained 8.47 g of citric acid, 3.22 g of NaOH and 2.18 g of HCl per liter, the intermediate pH buffer ($p\text{H} = 6.2$) contained 12.53 g of citric acid and 6.32 g of NaOH per liter, and the high pH buffer ($p\text{H} = 9.48$) contained 3.81 g of di-sodiumtetraborat per liter. The pH of the untreated D\textsubscript{2}O was around 5.5. The slight degree of acidity is attributed to solution of CO\textsubscript{2} from the atmosphere.

Bentheim sandstone cores with a diameter of 16 mm were cast into an impermeable epoxy layer, thereby increasing the diameter to 20 mm. The penetration of the epoxy in the core varied between 1 and 2 mm. The length of the cores is 60 mm. The porosity of a sample was determined through a mercury intrusion porosity (MIP) measurement yielding a porosity of 0.22 and a mean pore size of $33 \pm 10 \mu$m. In addition, a Bentheim core was scanned with a micro-CT (X-ray computer tomography) apparatus (Scanco Medical, type VivaCT 40) with a resolution of $10.5 \times 10.5 \times 10.5 \mu$m$^3$. An example image is given in Figure 6.2. The image clearly shows the irregular structure of the pore space, and that the rock contains a few pores with a size much greater than 33 $\mu$m. The pore volume of each core is about 2 ml. Bentheim is a water-wet rock, consisting mainly of quartz and little amounts of non-swelling clay (less than 1%, see Chapter 7).
Fig. 6.2: Micro-CT image of Bentheim sandstone showing the pore structure (black) and the solid material of a slice with a thickness of 10.5 µm.

Fig. 6.3: Schematic view of core holder and fluid injection set-up. The length \( L \) is 60 mm. The fluids are injected by either pump 1 (for oil and oil/TMOS) or pump 2 (for water). The differential pressure \( \Delta P \) over the core is measured with a differential pressure transducer connected to the tubing. The dashed lines indicate the slice positions in the NMR measurements.
6.2.2 Core holder and fluid injection system

A custom-made core holder was designed which fitted in the insert of the NMR apparatus. The holder is made of poly-ether-ether-ketone (PEEK) and can withstand pressures up to 23 bars. The temperature of the core holder was not controlled. During the experiment the cores are oriented vertically, and the inlet is at the bottom. The fluids are injected by two continuous-injection pumps (P500, Amersham Bioscience) connected to a computer. The differential pressure over the core holder was monitored with a Deltabar S pressure transducer (range: 0–1500 mbar). The tubing, between the core holder and the pressure transducer, introduces an additional pressure loss at a given flow rate. This pressure loss was calibrated and taken into account in the permeability measurements. A schematic view of the set-up is given in Figure 6.3. For the shut-in step, during which the reactive mass transfer is monitored through the NMR measurements, the cores are taken out of the core holder, sealed and put in a second sample holder. In this sample holder, made of polyvinylchloride (PVC), a fluorocarbon fluid (Galden™ HT135, manufactured by Solvay Solexis) with a regulated temperature is circulated so that the temperature of the sample can be controlled. The fluid is invisible to the NMR set-up and the temperature can be controlled between 10 and 65 °C with an accuracy of about 1 degree.

6.2.3 NMR apparatus and methods

A 0.95 Tesla NMR scanner was used to perform the NMR experiments. The scanner is equipped to measure both hydrogen, at a frequency of 40.5 MHz, as well as deuterium, at a frequency of 6.21 MHz. The set-up consists of an electromagnet with a vertical, narrow-bore insert with an inner diameter of 31 mm. A single rf coil is used with two different front-end rf circuits for $^1$H, respectively $^2$H. Switching between the two circuits is automated and takes less than a second, allowing for a fast sequential NMR measurement of hydrogen and deuterium. The insert is capable of producing a static magnetic gradient up to 0.2 T m$^{-1}$ in the vertical direction. The position of the core holder and sample holder is controlled by a stepper motor.

The sequences used for the experiments and details about the methods were discussed in Chapter 2. $T_1$ of the hydrogen content in the oleic phase is measured with a saturation recovery sequence to determine the TMOS concentration in oil, $T_2$ of the aqueous phase is measured with a Carr-Purcell-Meiboom-Gill (CPMG) sequence to monitor the progress of gelation. In this case $T_2$ is measured for the deuterium content. A 1D static magnetic gradient is used. Due to the relatively low signal to noise ratio for deuterium the signal is averaged 64 times. The acquisition time for a $T_2$ measurement in a single slice is about 4 minutes. The gradient strength was 0.030 T m$^{-1}$ and 0.015 T m$^{-1}$ for $^1$H, respectively $^2$H. In each experiment five equally-spaced slices were considered. The slice positions along the vertical direction were: -25 mm, -12.5 mm, 0 mm, 12.5 mm and 25 mm with respect to the center of the cores (see Figure 6.3). The relaxation times were acquired for each slice by using and averaging the part of the signal profile corresponding to a thickness of 3.1 mm. The saturation recovery data were analyzed and fitted with mono-exponential decay functions yielding the relaxation times $T_1$. The CPMG data were analyzed with the inversion routine CONTIN [66] to give quasi-continuous $T_2$ spectra, consisting of one
Table 6.1: Fluid injection steps in the core experiments.

<table>
<thead>
<tr>
<th>step</th>
<th>description</th>
<th>final saturation</th>
<th>permeability parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>main procedure:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>water injection</td>
<td>$S_w = 1$</td>
<td>$K_{abs}$</td>
</tr>
<tr>
<td>2</td>
<td>primary drainage (oil)</td>
<td>$S_w = S_{wi}$</td>
<td>$k_{ro}$</td>
</tr>
<tr>
<td>3</td>
<td>secondary imbibition (water)</td>
<td>$S_w = 1 - S_{or}$</td>
<td>$k_{rw}$</td>
</tr>
<tr>
<td>4</td>
<td>secondary drainage (oil)</td>
<td>$S_w = S_{wi}$</td>
<td>$k_{ro}$</td>
</tr>
<tr>
<td>5a</td>
<td>TMOS/oil injection</td>
<td>$S_w = S'_{wi}$</td>
<td>-</td>
</tr>
<tr>
<td>5b</td>
<td>shut-in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>oil injection</td>
<td>$S_w = S^*_{wi}$</td>
<td>$k^*_{ro}$</td>
</tr>
<tr>
<td>7</td>
<td>water injection</td>
<td>$S_w = 1 - S_{or}$</td>
<td>$k^*_{rw}$</td>
</tr>
<tr>
<td>alternative procedure:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>oil injection</td>
<td>$S_o = 1$</td>
<td>$K_{abs}$</td>
</tr>
<tr>
<td>2</td>
<td>TMOS/oil injection</td>
<td>$S_o = 1$</td>
<td>-</td>
</tr>
<tr>
<td>3a</td>
<td>primary imbibition</td>
<td>$S_o = S_{or}$</td>
<td>-</td>
</tr>
<tr>
<td>3b</td>
<td>shut-in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>water injection</td>
<td>$S_o = S_{or}$</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>oil injection</td>
<td>$S_o = 1 - S_{wi}$</td>
<td>-</td>
</tr>
</tbody>
</table>

hundred points on a logarithmic $T_2$ axis (see Chapter 2).

6.2.4 Experimental procedure

In each experiment a dry core was saturated under vacuum with normal heavy water or the buffered solutions, after which it was placed in the core holder. Subsequently, several fluid injection steps were performed during which the differential pressure was monitored and the (relative) permeabilities were determined. The steps are summarized in Table 6.1. In the first four steps the amount of fluids injected varies between 10 and 20 pore volumes (PV) per step. The flow rate was adjusted during each step such that the differential pressure did not exceed 1500 mbar. The absolute permeability, $K_{abs}$, of the core was determined in step 1. Primary drainage of the core was done in step 2 through the injection of pure oil. Stabilization of the differential pressure was always observed after injection of 10 to 20 PVs, indicating the core was at, or at least close to irreducible water saturation conditions ($S_w = S_{wi}$) and the relative permeability, $k_{ro}$, was determined. Similarly, water was injected in a secondary imbibition cycle (step 3) and the relative permeability, $k_{rw}$, at residual oil saturation conditions ($S_w = 1 - S_{or}$) was determined. Secondary drainage was applied in step 4 in order to obtain a state of irreducible water saturation again and to prepare the initial conditions before injecting the TMOS/oil mixture in step 5a. Between each step the amount of D$_2$O in five different slices and in absence of flow was determined through an NMR $T_2$ measurement as described in the previous section. This was done to measure the saturation profiles.
The amount of TMOS/oil mixture injected in step 5a was either 2 or 4 ml (about 1 to 2 PV) and was injected with a flow rate \( Q \) equal to 1 ml min\(^{-1}\). During the injection the mixture displaces the existing oil phase. Due to the difference in viscosity between the mixture and pure oil, which is about two times more viscous than the mixture, a gradual drop in differential pressure was observed while the oil was being displaced by the mixture. After injection, the core was quickly taken out of the core holder, sealed and put into the PVC sample holder which was preheated at either 25 °C or 50 °C. The NMR measurements were subsequently started with a delay of about 3 minutes after the injection of the mixture was ended. Continuous \( T_1 \) and \( T_2 \) measurements were performed for at least 20 hours. In case the temperature of the sample holder was 50 °C the sample needed to warm up from room temperature, which took about 30 minutes. This implies that for these experiments the relaxation times acquired in the initial 30 minutes of the experiment were affected by the temperature change. At the end of the shut-in period the core was removed from the PVC sample holder and put back again in the core holder. The final steps consisted of oil injection (step 6) followed by water injection (step 7) and the post-treatment relative permeabilities, \( k_{r_o}^* \) and \( k_{r_w}^* \), were determined.

Two experiments were done with an alternative preparation scheme (see Table 6.1). The cores were initially prepared at full oil saturation conditions. Several PVs of TMOS/oil were injected to displace the oil with the mixture. Subsequently, 4 ml of D\(_2\)O was injected (step 3a) in a primary imbibition cycle yielding the condition of residual oil, where the oil contains 20 vol\% of TMOS, followed by a shut-in period (step 3b). The final steps consisted of water injection (step 4) followed by oil injection (step 5a). An overview of all core injection experiments, listing the main experimental parameters, is given in Table 6.2.

### 6.3 Results and discussion

#### 6.3.1 NMR relaxation times of fluids and gels in bulk

The longitudinal relaxation time \( T_1 \) as a function of temperature was calibrated for the mineral oil and for mixtures of oil and TMOS with volume fractions of 0.20 and 0.40, respectively. The results are shown in Figure 6.4. For the pure oil \( T_1 \) is 154 ms at 15 °C and increases with temperature to 440 ms at 55 °C. As the TMOS concentration is increased \( T_1 \) of the mixture increases accordingly. In case of 20 vol\% TMOS in oil \( T_1 \) is 359 ms at 15 °C and increases to 700 ms at 55 °C, and for the 40 vol\% mixture \( T_1 \) is 595 ms at 15 °C and increases to 1130 ms at 55 °C.

The transverse relaxation time \( T_2 \) was calibrated for bulk gels that were prepared by mixing TMOS with heavy water, \( i.e. \) pure D\(_2\)O and the buffered solutions. The results were discussed in Chapter 4. \( T_2 \) is shorter for the gels than for bulk D\(_2\)O. The main contribution to the reduction in \( T_2 \) is due to the interaction (\( e.g. \) adsorption) of the D\(_2\)O molecules with the silica content. In case of a gelling solution \( T_2 \) is initially similar to that of bulk D\(_2\)O but decreases as the TMOS hydrolyzes and combines into silica clusters. The final reduction in \( T_2 \) increases with increasing initial TMOS content of the gelling solution.
Table 6.2: Overview of the core injection experiments and core properties. \( V_{\text{mix}} \) is the volume of TMOS/oil injected before shut-in, \( T \) is the temperature of the core during shut-in and \( K_{\text{abs}} \) is the absolute permeability. The relative permeabilities \( k_r^o \) and \( k_r^w \) are with respect to the end-point saturations. The residual resistance factor (RRF, see Section 6.3.5) was determined for oil and water after the shut-in step.

<table>
<thead>
<tr>
<th>label</th>
<th>( V_{\text{mix}} ) [ml]</th>
<th>buffer (pH)</th>
<th>( T ) [°C]</th>
<th>( S_{\text{wi}} )</th>
<th>( K_{\text{abs}} ) [μm²]</th>
<th>( k_r^o ) [-]</th>
<th>( k_r^w ) [-]</th>
<th>RRF(_o) [-]</th>
<th>RRF(_w) [-]</th>
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</thead>
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<tr>
<td>A01</td>
<td>2</td>
<td>no buffer</td>
<td>25</td>
<td>( S_{\text{wi}} )</td>
<td>1.4</td>
<td>0.65</td>
<td>0.30</td>
<td>1.4</td>
<td>3.6</td>
</tr>
<tr>
<td>A02</td>
<td>2</td>
<td>no buffer</td>
<td>50</td>
<td>( S_{\text{wi}} )</td>
<td>1.5</td>
<td>0.60</td>
<td>0.33</td>
<td>1.5</td>
<td>27</td>
</tr>
<tr>
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<td>( S_{\text{wi}} )</td>
<td>1.5</td>
<td>0.55</td>
<td>0.35</td>
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<td>( S_{\text{wi}} )</td>
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<td>( S_{\text{wi}} )</td>
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<td>0.26</td>
<td>3.2</td>
<td>6.6</td>
</tr>
<tr>
<td>A06</td>
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<td>0.26</td>
<td>1.9</td>
<td>3.2</td>
</tr>
<tr>
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<td>6.20</td>
<td>50</td>
<td>( S_{\text{wi}} )</td>
<td>1.6</td>
<td>0.81</td>
<td>0.31</td>
<td>1.4</td>
<td>6.0</td>
</tr>
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<td>A09</td>
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<td>25</td>
<td>( S_{\text{wi}} )</td>
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<td>0.66</td>
<td>0.36</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>A10</td>
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<td>9.48</td>
<td>50</td>
<td>( S_{\text{wi}} )</td>
<td>1.3</td>
<td>0.64</td>
<td>0.35</td>
<td>2.0</td>
<td>5.4</td>
</tr>
<tr>
<td>B01</td>
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<td>no buffer</td>
<td>25</td>
<td>( 1 - S_{\text{or}} )</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B02</td>
<td>4</td>
<td>no buffer</td>
<td>50</td>
<td>( 1 - S_{\text{or}} )</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

Fig. 6.4: Relaxation time \( T_1 \) of TMOS/Isopar V (oil) mixtures as a function of temperature. The concentration of TMOS is indicated in the legend.
6.3. Results and discussion

Fig. 6.5: Transverse relaxation time spectra of $^2$H content in middle slice of the core in experiment A03.

6.3.2 NMR relaxation times of fluids in sandstone

The transverse relaxation behavior of D$_2$O in the Bentheim rock at room temperature and at full water saturation was measured in each experiment after the initial saturation cycle (step 1). The spin echo trains were inverted with the CONTIN procedure, already described in Chapter 2, to obtain the $T_2$ spectra. In Figure 6.5 the $T_2$ spectrum is shown for the middle slice of the core in experiment A03. A main broad peak is found with its maximum at $T_2 = 0.247$ s. A smaller peak is found near 0.037 s. In terms of the area under the peaks the smaller peak contributes only to 6% of the total area. The weighted mean $T_{2,AV}$, defined as

$$T_{2,AV} = \frac{\int T_2 P(T_2) dT_2}{\int P(T_2) dT_2},$$

(6.1)

where $P(T_2)$ is the distribution function of $T_2$, is equal to 0.246 s, which indicates that the smaller peak contributes only slightly to the overall relaxation rate. Similar spectra were acquired for all other slices and all other cores. The average contribution of the main peak was 95 ± 1%. The average of the $T_2$ values derived from the maximum of the main peak was 0.25 ± 0.01 s. The average of the $T_2$ values derived from the maximum of the secondary peak was 0.025 ± 0.006 s. Drainage of the core through the injection of oil (step 2) results in lower signal intensities for $^2$H. The magnitude (or area) of the main peak is reduced by 79%. The secondary peak is broadened, which is attributed to a reduced signal-to-noise ratio, but the area is unchanged. The weighted mean $T_{2,AV}$ is reduced to 0.192 s. Secondary imbibition (step 3) leads to an increase of the magnitude of the main peak to 71% of the original magnitude (step 1), and $T_{2,AV}$ increases to 0.226 s. Finally, secondary drainage results in a reduction of the magnitude of the main peak to 19% of the original magnitude, and $T_{2,AV}$ decreases to 0.170 s. Throughout each cycle the
area of the small peak remained approximately constant. Similar spectra were observed for the other slices. After secondary drainage the combined $T_{2,AV}$ for all slices was 0.19 ± 0.03 s, and the saturation $S_{wi}$ derived from the signal intensities was 0.24 ± 0.04.

Three separate cores were prepared at full water saturation, irreducible water saturation, and full oil saturation, respectively. This was done in order to measure the relaxation times as a function of temperature and to compare the relaxation times to those of the bulk liquids. The results of the $^2$H-NMR measurements are presented in Figure 6.6. With respect to bulk $T_1$ of D$_2$O inside the core at $S_w = 1$ is reduced by about 10%. The weighted-mean $T_{2,AV}$ is reduced by roughly a factor of 2.

The magnetic susceptibility of the Bentheim sandstone, which consists for >99% of quartz, was determined with a superconducting quantum interference device (SQUID). The rock is mostly diamagnetic with a susceptibility of $-1.22 \times 10^{-5}$, but a small ferromagnetic response was observed, which could be due to contamination through the sawing of the sample. The magnetic susceptibility of (normal) water is $-9.0 \times 10^{-6}$ [67]. The susceptibility difference is small and because of the low gyromagnetic ratio of deuterium, the difference in the magnitude of the reduction between $T_1$ and $T_{2,AV}$ cannot be explained by internal magnetic field gradients. The reduction of the relaxation times for the D$_2$O molecules in the rock is mainly due to adsorption of the molecules onto the internal solid surface, and partly due to interaction with paramagnetic impurities, e.g. with aluminum present in the little amount of clay in the rock. The difference in $T_1$ and $T_{2,AV}$ is attributed to a difference in surface relaxivity. The small secondary peak in the $T_2$ spectra indicates that the surface relaxation is not completely averaged out by diffusion, i.e. the spins are not in the fast diffusion regime (see Brownstein and Tarr [119]). Due to the relatively large pores (in the order of 1–100 micron) the spins are in the intermediate
6.3. Results and discussion

![Graph showing longitudinal relaxation time $T_1$ of the $^1$H content measured during shut-in (step 5b) in five different slices of the core in experiment A03.](image)

**Fig. 6.7:** Longitudinal relaxation time $T_1$ of the $^1$H content measured during shut-in (step 5b) in five different slices of the core in experiment A03.

diffusion regime, so that higher order relaxation modes are expected. Further elaboration about the relaxation mechanisms in the wetting phase is out of the scope of this thesis. The longitudinal relaxation time $T_1$ of the hydrogen content in the rock (not shown here), carried by the oil, was not reduced with respect to that of bulk oil. Apparently, the oleic molecules do not adsorb onto the surface.

### 6.3.3 Mass transfer of TMOS

**Results of experiment A03**

The measurement of the average TMOS concentration in the oleic phase during shut-in (step 5b) in experiment A03 is demonstrated in this section. Before the injection of the TMOS solution the core was prepared at irreducible water conditions, such that $S_w = S_{wi} = 0.24 \pm 0.04$ (as determined by the $^2$H signal). Subsequently, 4 ml (about 2 PV) of TMOS/oil mixture was injected with an initial concentration $\phi_T = 0.20$. The continuous measurement of $T_1$ of the $^1$H content in the five slices was started within three minutes after TMOS/oil injection. The temperature in the sample holder was 25 °C. The results are shown in Figure 6.7 for the first 10 hours of the experiment. Between each measured slice the total delay time is about 5 minutes, which is small compared to typical mass transfer times. As a consequence, the first data point in the fifth slice ($z = 25.0$ mm) was acquired half an hour after the injection ended. The first acquired relaxation time in the first slice is $T_1 = 0.393 \pm 0.003$ s, which corresponds to a concentration $\phi_T = 0.168 \pm 0.008$, assuming that the $^1$H content is still exclusively present in the non-wetting, oleic phase. The initial values for $T_1$ of the consecutive slices were lower, especially in the fifth slice close to the outlet of the core, indicating lower average concentrations than in the
Fig. 6.8: Derived concentration of TMOS in the oleic phase, $\phi_T$, in five different slices of the core in experiment A03 during shut-in (step 5b). The concentration is based on the average $T_1$ of the total $^1$H content and is therefore affected by the presence of hydrogen in the aqueous phase.

first slice. This can be explained by assuming that the mixture may not have completely displaced the existing oil during placement, despite the injection of 2 PV of mixture. After the initial 10 hours, the $T_1$ in all slices becomes nearly constant around $T_1 = 0.223 \pm 0.006$ s, up to the total measurement time of 39 hours.

Due to the mass transfer of TMOS from the oleic to the aqueous phase, part of the total $^1$H content, carried by the TMOS molecules, transfers accordingly between both phases. The saturation recovery sequence measures the recovery of the longitudinal magnetization of all $^1$H atoms in the liquid phases. As long as the fraction of $^1$H is low in the aqueous phase, which is the case at the beginning of the shut-in process, the acquired $T_1$ represents the effective $T_1$ of the TMOS/oil phase and the concentration $\phi_T$ can be determined using the calibration results for the bulk mixtures. Direct determination of $\phi_T$ in the five slices using the calibration of $T_1$ of the oil/TMOS mixtures yields the concentration profiles shown in Figure 6.8.

Effect of hydrogen in aqueous phase on determination of $\phi_T$

As the TMOS progressively transfers to the aqueous phase, the $^1$H content in water increases. The measured $T_1$ is a weighted average of the $T_1$ of the various species containing hydrogen. The longitudinal magnetization $M_z(t)$ can be described by

$$M_z(t) = M_0 \left[ 1 - f \exp \left( -\frac{t}{T_{1,o}} \right) - (1 - f) \exp \left( -\frac{t}{T_{1,w}} \right) \right], \quad (6.2)$$
6.3. Results and discussion

Fig. 6.9: Derived mono-exponential relaxation time $T_1$ from reconstructed saturation recovery profiles for a binary system. $T_{1,o}$ of the hydrogen in the oleic phase is 0.20 s. $T_{1,w}$ of the hydrogen in the aqueous phase is varied between 0 and 4 s. The fraction, $f$, of the hydrogen protons in the aqueous phase is indicated in the legend. The length of the saturation recovery profiles was 3 seconds.

where $M_0$ is the equilibrium magnetization of all the hydrogen spins, $f$ is the fraction of hydrogen in the oleic phase (with respect the amount of hydrogen in both phases), $T_{1,o}$ is the effective $T_1$ of the oleic phase from which the concentration $\phi_T$ should be derived, and $T_{1,w}$ is the effective $T_1$ of all hydrogen species in the aqueous phase. The latter changes throughout the experiment as the gelation reactions and mass transfer proceed. The calibration measurements of the gel samples indicated that $T_{1,w}$ in the final stages of the gel process is about 3 to 4 s in bulk gels. The fraction $f$ can be calculated directly if one assumes that the mass transfer at each location in the core commences only after the injection step was ended, so that $f(t = 0) = 1$. In case of full transfer of TMOS the final fraction $f$ is derived from the initial volume fraction of TMOS, i.e. $\phi_T(0) = 0.20$, yielding $f = 0.15$. The hydrogen number density of the oil was calculated by considering the molecular volume and number of hydrogen atoms of $n$-hexadecane.

The effect of the hydrogen present in the aqueous phase on the measured $T_1$ was estimated by numerically constructing saturation recovery profiles (with the same echo spacing as in the experiment), using Eq. 6.2, and fitting those profiles with a single exponent. The relaxation time of the oleic phase, $T_{1,o}$, was set to 0.20 s which is the $T_1$ of oil without TMOS at a temperature of 25 °C, and $T_{1,w}$ was varied between 0 and 4 s. The obtained overall $T_1$ is shown in Figure 6.9 for three different fractions, i.e. $f = 0.05$, $f = 0.15$ and $f = 0.25$. Clearly, the difference between $T_1$ and $T_{1,o}$ increases with increasing fraction $f$. Due to the finite length of the saturation recovery profiles, which is three seconds, the overall $T_1$ increases with increasing $T_{1,w}$ up to a certain maximum at $T_{1,w} < 4$ s. When $f = 0.15$ the overall $T_1$ has a maximum of 0.234 s near $T_{1,w} = 1$ s,
6. Coupled mass transfer and gelation of TMOS in porous materials

Table 6.3: Fit results for the mass transfer rate $\alpha_T$ and the gelation rate $\kappa$.

<table>
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<th>label</th>
<th>buffer (pH)</th>
<th>$T$ [°C]</th>
<th>$\alpha_T$ [h$^{-1}$]</th>
<th>$\kappa$ [h$^{-1}$]</th>
</tr>
</thead>
<tbody>
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<tr>
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<tr>
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</tbody>
</table>

which would correspond to a concentration of $\phi_T = 0.03$. The final plateaus observed in the uncorrected concentration profiles of $\phi_T$, for all experiments, lie between $\phi_T = 0.02$ and $\phi_T = 0.07$. It was found in two-phase bulk experiments (see Chapters 2 and 4) that the TMOS continues to transfer from the oleic to the aqueous phase even when gelation of the aqueous phase has already occurred. Assuming that the transfer of the TMOS in the porous material also tends to a complete transfer the high plateaus of $\phi_T$ are caused by apparently high values of $T_1$ due to the contribution of hydrogen in the aqueous phase.

Mass transfer rates

In order to characterize the mass transfer rate of TMOS during the shut-in period the obtained time dependences of the concentration profiles for all slices were combined to a single time dependence and smoothed. This yields a profile that represents an average profile for the experiment. Subsequently, the average profile is fitted with a first-order exponential decay function, given by

$$\phi_T(t) = A \exp(-\alpha_T t) + B,$$  \hspace{1cm} (6.3)

where $A$ is the initial concentration, $\alpha_T$ is the mass transfer rate, and $B$ is an offset. The average profiles for experiments A03, A05, A07 and A09 (which were done at 25 °C) are given in Figure 6.10. Again, the concentration profiles show a non-zero plateau, due to the presence of $^1$H in the aqueous phase, which affects the measurement of $\phi_T$. Except for experiment A07 the initial points of the concentration profiles are well below $\phi_T = 0.20$, which is probably due to a high mass transfer rate during injection of the chemical before the shut-in period. For now we focus on the typical mass transfer rate during shut-in. The profiles are adequately fitted with the exponential decay function (Eq. 6.3). The resulting mass transfer rates $\alpha_T$ for all experiments are listed in Table 6.3. At 25 °C the mass transfer rate is on the order of 0.5 h$^{-1}$ for all experiments except A05, for which the mass transfer rate is 8.1 ± 0.8 h$^{-1}$. The mass transfer is driven by the degree
6.3. Results and discussion

[Graph showing concentration of TMOS in the oleic phase, $\phi_T$, as a function of time and averaged over all slices.]

**Fig. 6.10**: Concentration of TMOS in the oleic phase, $\phi_T$, as a function of time and averaged over all slices. The profiles were smoothed but not corrected for the effect of hydrogen present in the aqueous phase. The experiments were done at 25 °C and the pH of the aqueous phase was varied (see Legend).

of hydrolysis. At the lowest pH the rate of hydrolysis is the highest, and therefore the mass transfer is the fastest. The lowest values for $\alpha_T$ are found for the unbuffered and pH = 6.20 systems. It is noted that the pH of the aqueous phase in the unbuffered systems decreases to an unknown extent as the hydrolysis of TMOS proceeds. At 50 °C the mass transfer rate is increased roughly by a factor 2 in case of the unbuffered and pH = 6.20 systems. For the pH = 9.48 system $\alpha_T$ increased by a factor 4 to $2.9 \pm 0.3 \text{ h}^{-1}$. For the pH = 2.84 system (A06) the mass transfer was already completed within the dead time of the experiment, so that $\alpha_T > 20 \text{ h}^{-1}$. Exact quantitative comparison between the mass transfer results of the core experiments and the bulk experiments are not made due to the different spatial distribution and ratio of the liquid phases. However, like in the bulk (see Chapter 4) the mass transfer is predominantly driven by the hydrolysis reaction, the rate of which is strongly dependent on the pH of the aqueous phase, and on temperature, especially for the alkaline systems. In the acid-catalyzed system, with a pH around 3, the hydrolysis rate and the mass transfer rate are the fastest, like in the bulk experiments. At a pH of about 6, the hydrolysis rate should be minimum [33]. The mass transfer rates at a pH of 6.20 in the core experiments are similar to those for the unbuffered system, however, in the bulk it was found that the mass transfer was much faster in the unbuffered systems compared to the buffered systems at a pH of 5.5.
6. Coupled mass transfer and gelation of TMOS in porous materials

6.3.4 Gelation

Results of experiment A03

The measurement of the transverse relaxation behavior in the aqueous phase during shut-in (step 5b) in experiment A03 is discussed in this section. The continuous measurement of $T_2$ of the $^2$H content in the five slices was started within three minutes after the injection step. The spin echo trains, acquired with the CPMG sequence, were inverted with the CONTIN routine. Again, the weighted-mean $T_2$ as defined in Eq. 6.1 was used to characterize the average $T_2$ within each slice as a function of time. The results are shown in Figure 6.11 for the first 10 hours of the experiment. Between each measured slice the total delay time is about 5 minutes. As a consequence, the first data point in the fifth slice ($z = 25.0$ mm) was acquired half an hour after the injection was ended. The first data point in the first slice is found at $T_{2,AV} = 0.123$ s. The remaining values of $T_{2,AV}$ in the other slices and for the other time steps drop progressively to about 0.025 s.

The drop in $T_{2,AV}$ is due to the reaction of TMOS with the water molecules, i.e. due to the formation of methanol and due to the cross-linking silica aggregates. The effect of the gel reaction dominates the shortening of $T_{2,AV}$, compared to the effect of the surface relaxivity of the rock. However, the exact pore-scale distribution of the reacting TMOS and formed gel in the aqueous phase remains unclear, and the weighted-mean $T_2$ can only indicate an effective reaction rate and effective gel transition time. Based on the ratio of oil and water (derived from $S_w \approx 0.25$) and the initial concentration of TMOS ($\phi_T(0) = 0.20$), the final volume fraction of TMOS in the aqueous phase, assuming full mass transfer, is 38%. It was found in bulk experiments that at this concentration the resulting gel always percolated into a macroscopic gel for all buffers used. On the pore scale the

![Figure 6.11](image.png)

Fig. 6.11: Weighted-mean transverse relaxation time $T_{2,AV}$ of the $^2$H content in the aqueous phase measured during shut-in (step 5b) in five different slices of the core in experiment A03.
formed gel is likely to be inhomogeneous, i.e. the highest silica density is found in the water which is in direct contact with the non-wetting phase. In addition, after gelation some syneresis may occur, especially when the pH is low [123, 124].

**Gelation rates**

A similar procedure as was applied for the concentration profiles was applied to the $T_2$ profiles in order to yield a smooth and average $T_2$ profile for each experiment, so that the characteristic gelation rate and gel time could be determined. The average profiles for experiments A03, A05, A07 and A09 (which were done at 25 °C) are given in Figure 6.12. In order to assign a characteristic rate to the gelation reaction the $T_{2,AV}$ profiles were fitted with a mono-exponential decay function, given by

$$T_{2,AV}(t) = C \exp(-\kappa t) + D,$$

where $C$ is the initial $T_{2,AV}$, $\kappa$ is the gelation rate, and $D$ is an offset. The resulting characteristic gelation rates $\kappa$ for each experiment are given in Table 6.3. It can be observed in Figure 6.12 that the exponential function is adequately fitted to the initial decay in the first hour of the $T_{2,AV}$ profiles as well as to the final plateaus. The fit in the interval $1 < t < 3$ h is worse, except for the system with pH = 2.84. In the systems with pH = 2.84 and pH = 6.20 the initial values of $T_{2,AV}$ are found between 60 and 70 ms, which is well below the initial values for the pH = 9.48 and the unbuffered systems. This is due to the fast hydrolysis in the pH = 2.84 case, and the fast gelation in the pH = 6.20 case, respectively.
In bulk systems it was found that the initial decay of $T_2$ in the aqueous phase was equally fast for the $pH = 9.48$ system and the $pH \approx 6$ system. Here the relatively slow decay of $T_{2,AV}$ in the $pH = 9.48$ case suggests that the gel reaction is slower compared to the unbuffered case and the $pH = 6.20$ case. However, the relaxation time $T_{2,AV}$ is an average of the $T_2$ spectrum obtained with the inversion routine. It was found that especially for the $pH = 9.48$ case (experiments A09 and A10) the $T_2$ spectra showed a relatively high contribution of the long $T_2$ peak (around 100 ms) throughout the measurement interval, which also explains the high plateau value of $T_{2,AV}$ around 50 ms. This is indicative of a fast and inhomogeneous gelation of the water in contact with the oleic phase, so that a large amount of water in the aqueous phase has not turned into a gel. The effect was observed within each slice.

The fitted parameter $\kappa$ (see Table 6.3) reveals that, for a consistent set of conditions (experiments A03 through A10), the decay of $T_{2,AV}$ is the fastest for the $pH = 6.20$ system and the slowest for the acid-catalyzed system. Increasing the temperature from 25 °C to 50 °C for most systems results in an increase of $\kappa$ by roughly a factor of 2, except for the unbuffered systems, for which the inconsistent results cannot be explained at this point. The acid-catalyzed system appears to be most sensitive to temperature in terms of $\kappa$. The low values of $\kappa$ of about 0.5 h$^{-1}$ in the experiments B01 and B02, compared to the experiments A01 through A04, are expected since the cores were prepared at residual oil (B01 and B02). Therefore, the ratio of water/oil is much higher and the concentration of TMOS – which partitions between both phases – in the aqueous phase is lower than that in the experiments A01 through A10.

### 6.3.5 Effect of treatment on permeability

The absolute permeability $K_{abs}$ of each core is listed in Table 6.2. The permeability for water at full water saturation was found to vary between 1.3 and 2.0 $\mu$m$^2$. It is noted that despite the use of vacuum in the initial saturation step a slight amount of air was reintroduced in the cores when they were put in the core holder and the tubing was connected. The presence of air bubbles, as a non-wetting phase, in the core lowers the apparent absolute permeability. Some of the experiments showed a high relative permeability to oil ($k_{ro} \approx 0.8$) in the primary drainage cycle. Since the oil would replace the air bubbles present, this indicates that the measured $K_{abs}$ should be higher and $k_{ro}$ lower. However, quantitative corrections cannot be made. The effect of the gel treatments is expressed in the residual resistance factor, $RRF$, which is the ratio of the relative permeability for oil or water after treatment and the relative permeability before treatment. Both of these are based on the same $K_{abs}$ so that the accuracy of the absolute value becomes less important. The relative permeability $k_{rw}$ after the secondary imbibition cycle (step 3) was found to vary between 0.21 and 0.36, and the relative permeability $k_{ro}$ after the secondary drainage cycle (step 4) was found to vary between 0.51 and 0.84. The much lower water relative permeability compared to the oil relative permeability is expected in a water-wet core [118].

In the post-treatment injection steps (step 6 and step 7) the differential pressure showed a highly erratic behavior at a given flow rate during the initial 10 to 20 minutes. This is attributed to displacement of or damage to the gel which is formed in the pore
space by the flow of oil or water, though the flow rate was always limited to keep the pressure below 1500 mbar. Due to the mass transfer of TMOS during shut-in the volume of the non-wetting oleic phase decreases by about 20% and the volume of the aqueous phase increases by the same amount. The injection of oil in step 6 is therefore likely to result in a partial displacement of the gelled water. The water that is injected after treatment in step 7 will either displace the gel, be forced to flow between the gel and the non-wetting phase or between the gel and the pore wall, or will channel through the gel. The intrinsic permeability of the wet gel is typically between 1 and 100 nm² [123, 125] so that the contribution of flow through undamaged gel can be neglected. It was observed in the experiments that the differential pressure stabilized at a fixed flow rate after the initial period of 10 to 20 minutes. Subsequently, the oil and water relative permeability were determined in step 6, respectively step 7, by using $K_{abs}$ determined in the first injection step. One could argue that the pore structure is modified by the formed silica gel, and that the absolute permeability changes accordingly. Nevertheless, the original $K_{abs}$ was used in order to quantify the effect of the treatment on the relative permeabilities.

The residual resistance factors for oil ($RRF_o$) and water ($RRF_w$) are given in Table 6.2. The gel treatment always led to a reduction of the permeability to oil. The measured parameter $RRF_o$ varied between 1.4 and 2.0 for most of the experiments. Slightly higher values ($RRF_o \approx 3$) were found when the acid buffer was used. Acid-catalyzed gels are prone to syneresis [123, 124] so that the silica density and the stiffness are increased. This may explain the relatively high resistance to flow even for the non-wetting phase. The values for $RRF_w$ are within a broad range between 1.9 and 27. The unusually high value for experiment A02 might be due to partial blocking of the outlet by the gel. Nevertheless, in each experiment $RRF_w$ was found to be 1.5 to 4 times higher than $RRF_o$, and therefore the gel treatment effectively results in a permeability reduction for water without a significant reduction of the oil relative permeability. The significant variation in $RRF_w$ suggests that the flow reduction is sensitive to parameters other than the conditions during the gel formation (pH and temperature). The relative permeabilities were not measured in experiments B01 and B02.

### 6.4 Conclusion

In situ characterization of the coupled mass transfer and gelation of TMOS within a natural porous material under two-phase conditions was achieved with the bi-nuclear NMR measurements on TMOS/oil and heavy water. Despite the uncertainty, for each slice and time step, in the measured average TMOS concentration $\phi_T$ of about $\pm 0.05$, the TMOS appears to transfer almost completely from the oleic to the aqueous phase on a time scale of less than an hour to more than 5 hours. Like in the bulk, the mass transfer of TMOS is driven by the rate of hydrolysis. Around pH = 6 and for the unbuffered systems the rate is the lowest, whereas the hydrolysis rates, and thus the mass transfer rates, are increased in the acid- and base-catalyzed systems. At a temperature of 50 °C the rates are increased roughly by a factor 2 with respect to a temperature of 25 °C. The characteristic gelation times, derived from the average $T_2$ versus time profiles, revealed that the gelation rates were the highest for the pH = 6.20 systems (gel time on the order
of 1 hour), and the lowest for the $pH = 2.95$ systems (gel time up to 10 hours). However, the exact pore-scale mechanisms of gelation remain unclear and, consequently, the decay of the average $T_2$ in water only indicates a characteristic reaction rate. It was found that, due to the gel treatment, for each sandstone core the relative permeability to water was reduced more than that to oil. The effect of gel, which is formed under single phase conditions, on the permeability of the rock is considered in the next chapter.
Permeability reduction in porous materials by in situ formed silica gel

The effect of in situ formed silica gel on the permeability of a porous material was investigated experimentally using the method of beam bending. The permeability and Young’s modulus of gel-treated sandstones and of gel rods were measured. The gel structure was varied by varying the concentration of TMOS in solution and the pH of the water used. The permeability and modulus were extracted from a detailed analysis of the load relaxation profiles obtained in the experiments. The permeability of the gels decreases with increasing silica content and acid-catalyzed gels exhibit a significantly lower permeability than base-catalyzed gels. The permeability of the sandstone samples is reduced by a factor $10^4$ due to the gel treatment.

7.1 Introduction

The method of beam bending [126, 127] was employed to measure the permeability of TMOS-based silica gels and to measure the permeability of a porous material treated with gel that was formed in situ under single phase conditions. With respect to a downhole gel treatment (see Chapter 1), the situation of permeability reduction due to formation of gel under single phase conditions is, for example, found in a water-bearing layer near the injection front of the TMOS solution.

Gelling solutions of TMOS, methanol and water were imbibed in dried sandstone plates and allowed to react and cure. Gel rods were made from the sol-gel solutions in order to compare the intrinsic permeability of the gel with the permeability of the treated rock samples. In the beam bending method a saturated porous material, immersed in a liquid bath, is subject to three-point bending. Upon bending of the sample a hydrodynamic pressure gradient builds up and the pore liquid flows until the pressure is equilibrated. A constant deflection is imposed on the sample and the load (force) required to maintain that deflection is measured. The load relaxes with a typical decay time from which the permeability can be derived. The beam bending technique is especially adequate for low-permeability materials such as silica gels [126], porous glass [128] or cement paste [129]. In addition, the beam bending method concurrently yields the elastic moduli and the degree of viscoelasticity (if any), both of which are of interest with respect to the mechanical properties and performance of the gels and stones. The purpose of this work is to investigate whether the gel effectively fills the pore space and whether the reduction of the overall permeability is sensitive to parameters like pH and TMOS concentration.
7. Permeability reduction in porous materials by in situ formed silica gel

Fig. 7.1: Schematic of 3-point beam bending. The deflection $\Delta$ is sustained with a force $W$. The diameter of the cylindrical beam is $d$, and the distance between the supports is $L$.

7.2 Theoretical background

For a cylinder with diameter $d$ made of an elastic porous material, the load $W$, needed to sustain a constant deflection $\Delta$ (see Figure 7.1), is given by [130]

$$
\frac{W(t)}{W(0)} = R(t) = 1 - A + A \sum_{n=1}^{\infty} \frac{8}{\beta_n^2} \exp \left( -\frac{\beta_n^2 t}{\tau_R} \right),
$$

(7.1)

where $A$ is the amount of hydrodynamic relaxation, $\beta_n$ are roots of the Bessel functions $J_1(\beta_n) = 0$, and $\tau_R$ is the hydrodynamic relaxation time. In case of a gel the solid material comprising the porous body is usually very compliant such that compressibility effects in the system can be omitted. The amount of hydrodynamic relaxation $A$ is then simply a function of the Poisson ratio $\nu_p$, that is, $A = (1 - 2\nu_p)/3$. The hydrodynamic relaxation time $\tau_R$ is given by [128]

$$
\tau_R = \frac{(1 - 2\nu_p)\eta_L d^2}{4DG_p},
$$

(7.2)

where $\eta_L$ is the pore liquid viscosity, $D$ is the permeability and $G_p$ is the shear modulus of the (drained) porous system. The latter follows from Young’s modulus $E_p$ through the relation $E_p = 2(1 + \nu_p)G_p$. Young’s modulus is derived from the initial load $W(0)$ and the moment of inertia, $I = \pi d^4/64$, using the following equation

$$
E_p = \frac{W(0)(1 - A)L^3}{48\Delta I},
$$

(7.3)

where $L$ is the span in the three-point bending experiment.

For a rectangular isotropic beam (plate) of elastic porous material, with thickness $2a$ and width $2b$, the normalized load as a function of the reduced time $\theta = t/\tau_R$ is given by [131]

$$
\frac{W(\theta)}{W(0)} = R(\theta) = 1 - A + AS_1(\theta)S_2(\kappa\theta),
$$

(7.4)

where $\kappa = a^2/b^2$ and the functions $S_1$ and $S_2$ are given approximately by [132]

$$
S_1(\theta) \approx \exp \left[ -\left( \frac{6}{\sqrt{\pi}} \right) \left( \frac{\theta^{0.5} - \theta^{2.5}}{1 - \theta^{0.551}} \right) \right],
$$

(7.5)
In case the beam consists of rock, which has a much higher modulus than gel, the compressibility effects have to be taken into account. The parameter \( A \) is then replaced by

\[
A = \frac{\left(1 - 2\nu_p\right) \left(1 - \frac{K_p}{K_S}\right)^2}{1 - \frac{K_p}{K_S} + (1 - \rho) \left(\frac{K_p}{K_L} - \frac{K_p}{K_S}\right)},
\]

in which \( K_p \) is the bulk modulus of the drained network, \( K_S \) is the bulk modulus of the solid constituting the porous network, \( K_L \) is the bulk modulus of the pore fluid, and \( \rho \) is the volume fraction of the solid content. The hydrodynamic relaxation time \( \tau_R \) is related to the permeability \( D \) and the viscosity of the pore fluid \( \eta_L \) by

\[
\tau_R = \left\{ \frac{2(1 + \nu_p)}{3K_p} + \frac{1 - \rho}{K_L} + \frac{1}{K_S} \left[ \rho - \frac{4(1 + \nu_p)}{3} - \left(\frac{1 - 2\nu_p}{3}\right) \left(\frac{K_p}{K_S}\right) \right] \right\} \left(\frac{\eta_L \alpha^2}{D}\right). \tag{7.8}
\]

The bulk modulus \( K_L \) is known for most common liquids, and the bulk modulus \( K_p \) equals \( E_p/3(1 - 2\nu_p) \). The approximation \( K_p/K_S \approx \rho^2 \) can be used to estimate \( K_S \) [129].

Many materials, including aged gels that still contain a certain amount of water, show viscoelastic (VE) behavior. When the characteristic time of viscoelastic relaxation is at least an order of magnitude longer than the characteristic time of hydrodynamic relaxation, the total load relaxation \( W(t)/W(0) \) is adequately represented by the product of the hydrodynamic relaxation function \( R(t) \), as described above, and an uniaxial stress relaxation function, \( \Psi_{VE} \) [133]

\[
\frac{W(t)}{W(0)} = R(t)\Psi_{VE}(t). \tag{7.9}
\]

The function \( \Psi_{VE} \) is essentially an empirical function and can be inferred from experimental data. However, for many systems the VE relaxation can be adequately described by a stretched exponential:

\[
\Psi_{VE} = \exp \left[- \left(\frac{t}{\tau_{VE}}\right)^\alpha\right], \tag{7.10}
\]

where \( \tau_{VE} \) is the VE relaxation time and \( \alpha \) is a parameter \((0 \leq \alpha \leq 1)\).

### 7.3 Experimental section

#### 7.3.1 Materials

The Bentheim sandstone was obtained from a Bad-Bentheim quarry in Germany. Rectangular plates were sawed from a single block. The length and the width of the plates were 160 ± 5 mm and 25.2 ± 0.4 mm, respectively. The thickness of the plates varied...
between 8.05 and 10.10 mm. For each plate the thickness and width were checked at several positions on the plate surface. The precision of the thickness and width was about 0.05 mm. The sawed plates were dried at 60 °C for five days.

Bentheim is a quasi-homogeneous sandstone without distinct bedding planes or other form of anisotropy. Mercury intrusion porosimetry (MIP) on a same batch of Bentheim sandstone indicated that the sandstone has a narrow pore size distribution with an average pore size of $33 \pm 10 \, \mu m$ and a total porosity of about 0.22. The permeability of the rock with respect to water, which was measured on several cylindrical cores using a custom-made core injection set-up, was found to be $1.6 \pm 0.3 \, \mu m^2$. Bentheim sandstone is quartz-rich with little clay content. To test the presence of clays, small rock slabs were soaked in water and their length was monitored in a dynamic mechanical analyzer (DMA, type Perkin Elmer DMA 7e). In addition, the rock was analyzed in a scanning electron microscope (SEM, type FEI XL30 FEG-SEM) equipped for energy-dispersive X-ray spectroscopy (EDX, type PGT-IMIX PTS EDX). A fractured surface was coated with gold. The coating is needed to prevent the accumulation of static electric fields at the sample during imaging due to the electron irradiation. Another piece of rock was ground and analyzed using X-ray diffraction (XRD) in a Rigaku Miniflex apparatus.

TMOS was obtained from Acros Organics (99% pure). Deionized water was used for the hydrolysis reaction. The homogenization chemical used was methanol (Fisher Scientific, 99.9% pure). Ethanol (Pharmco, dehydrated, 200 Proof) was used to exchange with the mother liquid of the gels after curing. For the beam bending measurements on the sandstone samples the pore liquid was exchanged with glycerol (Acros Organics, 99+% pure).

Buffer solutions of the water were made by dissolving the following chemicals. The acid solution ($pH = 3.1$) contained 8.47 g of citric acid, 3.22 g of NaOH and 2.18 g of HCl per liter. The alkaline solution ($pH = 9.25$) contained 0.1 M of ammonium-hydroxide and 5.12 g per liter of ammonium-chloride (about 0.1 Molal). The latter was diluted with deionized water (with a ratio of 1:9) to yield a second alkaline solution with a $pH$ of 8.8.

### 7.3.2 Preparation of gels and rock samples

The sol-gel solutions were prepared by first mixing TMOS with methanol in various ratios to form homogeneous mixtures. The water (acid or alkaline) was added gradually to each mixture. The water/TMOS molar ratio was always equal to 4:1. The corresponding total volume fraction of TMOS in solution varied between 0.35 and 0.55. The solutions were homogenized by stirring during one minute. The solutions were cast in cylindrical Teflon molds with an inner diameter of $11.5 \pm 0.1 \, mm$ and a length of about 13 cm. After several days of curing at room temperature the gel rods were removed from the molds and immersed in ethanol with an excess volume of about 10 to 1 for at least one day, after which the gels were put into a second bath of fresh ethanol for several days. This procedure was applied to maximize the exchange of the mother liquid in the gels with ethanol, so that the viscosity of the pore liquid is known, and in order to minimize further aging of the gels and minimize the degree of viscoelasticity. Scherer showed that when the pore liquid is exchanged, using various alcohols, the measurement of the permeability
of a gel yields consistent results [126, 134]. The gel time of the sol-gel solutions was not systematically measured. However, the occurrence of gelation of each solution was verified by casting part of each solution in transparent vessels and checking the ability of the solution to flow 24 hours after preparation. All solutions gelled within 24 hours. The solutions prepared using the $p\text{H} = 9.25$ buffer gelled relatively fast within minutes or hours, depending on the TMOS concentration, and much faster than the solutions prepared with the diluted buffer ($p\text{H} = 8.8$). In the remainder of this work the degree of aging of the gels refers to combined curing and aging time of the gels with respect to the instant the solutions were prepared.

Gelling solutions, that were prepared as described above for the gel rods, were imbibed into the dry rock samples followed by complete immersion in the solution for ten seconds. The imbibition, driven by capillary rise, was initiated by slowly lowering the sandstone plates into the solution, such that the shortest dimension of the plates was directed vertically. The saturation of a sandstone plate was indicated by a color change of the rock surface as the solution imbibed, and was completed within ten seconds. Subsequently, the rock samples were tightly wrapped in several layers of aluminum foil. Plastic foil was wound around the aluminum. This way the evaporation of the gelling solution or drying of the resulting gel near the rock surface was minimized and the aluminum could easily be removed from the treated rock samples. For each TMOS concentration and $p\text{H}$ used (see Table 7.3) two separate rock samples were prepared in order to check the reproducibility. Similar exchange procedures used for the gels were applied to the rock samples. First the rock samples were immersed in pure ethanol for an extended period to arrest the curing. Next the samples were put into a mixture of ethanol and glycerol (50 vol%) to exchange part of the ethanol in the pores with glycerol. Finally, the samples were immersed in glycerol for several days in order to maximize the exchange of the pore liquid with glycerol. With respect to the overall pore volume of the rock samples the excess volume of the glycerol was about 25 to 1. The use of a high-viscosity liquid such as glycerol was necessary in order to prevent the hydrodynamic relaxation from being too fast with respect to the temporal resolution and accuracy of the beam bending method, since the rocks have high moduli on the order of 10 GPa.

### 7.3.3 Beam bending setup

An extensive description of the beam bending apparatus is given in Ref. [128]. Two equivalent set-ups were used, both of which were situated in an incubator. The first set-up (see Figure 7.2) was used for the gel measurements, which were done at room temperature. The temperature was stable during each run with fluctuations smaller than 1 °C. The second set-up was used for the rock sample measurements. The temperature was controlled to $26 \pm 0.5$ °C. Each set-up contains a stainless steel bath which was filled with ethanol for the gel measurements and glycerol for the rock sample measurements. The gel samples were aligned at a fixed position using V-notch supports consisting of 6.35-mm-diameter rollers set at an angle of 90° with respect to each other, and forming 45° angles with the horizontal plane. The pushrod, comprising an iron core and stainless steel hammerhead end was mounted onto the load cell. The load cell (SENSOTEC), with a capacity of ± 50 g, was mounted onto the stepper motor (UltraMotion). The displacement
of the pushrod was monitored through a linear-variable differential transformer (LVDT, Macrosensors). The span \((L)\) of the supports was 110 mm. The sandstone plates were supported by two different stainless steel supports. One consisted of a recessed ball, the other of a pivoting cylinder. This configuration was chosen to prevent torsion. The span in this case was 150 mm. A round-tipped pushrod (diameter = 6.3 mm) was used to bend the plates. A load cell with a capacity of \(\pm 1000\) g was mounted onto the stepper motor. In addition a 1000 g counter-weight was mounted on the pushrod.

![Stepper motor](image)

**Fig. 7.2:** Photo of beam bending set-up. A rectangular beam is placed in the bath.

The rock samples and gel rods were put in the bath at least 30 minutes in advance of the bending experiment in order to equilibrate thermally and mechanically. During bending deflections of about 1 or 1.5 mm were applied to the gels, whereas a deflection of about 35 \(\mu\)m was applied to the rock samples. The small deflection for the rock samples was chosen because of the limited load capacity of the system and in order to prevent the rock samples from cracking or breaking. Due to the small deflection with respect to the surface roughness – the grain size of the sandstone is on the order of 50 to 500 \(\mu\)m – the bending measurement is sensitive to the effect of slipping of the pushrod at the surface or slipping of the rock on the supports. Test measurements indicated that this effect occurred by yielding unrealistically low moduli \((E_p)\) for some samples and scattered results when a sample was repeatedly measured. Therefore the samples were preloaded with a net load of about 100 g prior to the equilibration period to promote a more stable settling of the rock and pushrod. The total load upon deflection is on the order of 1 kg.

### 7.4 Results and discussion

#### 7.4.1 Gels

**Gel properties**

Four series of gel rods were prepared. The TMOS concentration was varied in series I and IV. The concentration was kept fixed in series II and III, but extra salt, in the form of sodium-chloride (NaCl), was added in various concentrations, \(C_S\), up to 80 mMolal. The effect of additional salt on the gel properties was investigated in consideration of
application of the gel in natural reservoirs, since the water found in most reservoirs is saline. The properties of the gel rods are listed in Table 7.1.

Table 7.1: Properties of the gel rods and beam bending results. $\phi_{Si}$ is the estimated volume fraction of silica assuming full hydrolysis and condensation, and corrected for the volume contraction of the gel. The $pH$ listed is the $pH$ of the water used in the hydrolysis reaction. The parameter $C_S$ represents the amount of sodium-chloride (NaCl) added to the gelling solution.

<table>
<thead>
<tr>
<th>series</th>
<th>$\phi_{Si}$</th>
<th>$pH$</th>
<th>$C_S$ [mMolal]</th>
<th>aging time</th>
<th>$E_p$ [MPa]</th>
<th>$D$ [nm$^2$]</th>
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<tbody>
<tr>
<td>I</td>
<td>0.113 ± 0.007</td>
<td>3.1</td>
<td>0</td>
<td>43 h</td>
<td>5.9 ± 0.2</td>
<td>1.04 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>0.131 ± 0.008</td>
<td>3.1</td>
<td>0</td>
<td>43 h</td>
<td>12.2 ± 0.5</td>
<td>0.67 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.149 ± 0.009</td>
<td>3.1</td>
<td>0</td>
<td>43 h</td>
<td>22.8 ± 0.9</td>
<td>0.38 ± 0.02</td>
</tr>
<tr>
<td>II</td>
<td>0.123 ± 0.007</td>
<td>3.1</td>
<td>0</td>
<td>91 h</td>
<td>18.6 ± 0.7</td>
<td>0.66 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.123 ± 0.007</td>
<td>3.1</td>
<td>40</td>
<td>91 h</td>
<td>15.9 ± 0.6</td>
<td>0.72 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.123 ± 0.007</td>
<td>3.1</td>
<td>60</td>
<td>91 h</td>
<td>15.1 ± 0.6</td>
<td>0.76 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>0.123 ± 0.007</td>
<td>3.1</td>
<td>80</td>
<td>91 h</td>
<td>15.5 ± 0.6</td>
<td>0.72 ± 0.04</td>
</tr>
<tr>
<td>III</td>
<td>0.098 ± 0.005</td>
<td>9.25</td>
<td>0</td>
<td>72 h</td>
<td>6.9 ± 0.3</td>
<td>14.8 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>0.098 ± 0.005</td>
<td>9.25</td>
<td>40</td>
<td>72 h</td>
<td>7.3 ± 0.3</td>
<td>18.2 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>0.098 ± 0.005</td>
<td>9.25</td>
<td>60</td>
<td>72 h</td>
<td>7.0 ± 0.3</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>IV</td>
<td>0.078 ± 0.004</td>
<td>8.8</td>
<td>0</td>
<td>72 h</td>
<td>1.4 ± 0.1</td>
<td>40 ± 2</td>
</tr>
<tr>
<td></td>
<td>0.092 ± 0.005</td>
<td>8.8</td>
<td>0</td>
<td>72 h</td>
<td>2.9 ± 0.1</td>
<td>28 ± 2</td>
</tr>
<tr>
<td></td>
<td>0.100 ± 0.005</td>
<td>8.8</td>
<td>0</td>
<td>72 h</td>
<td>4.0 ± 0.2</td>
<td>20 ± 1</td>
</tr>
</tbody>
</table>

The parameter $\phi_{Si}$ is a measure for the total silica content of the alcogels based on the initial TMOS content and on the assumption that hydrolysis and condensation are complete. However, complete condensation implies the silica network would condense into non-porous quartz, which is not the case. Neither does the estimate account for possible washing out of polysiloxane molecules in the exchange process. Still, this measure is used to indicate the silica content of the gels. The values for $\phi_{Si}$ were corrected for volume contraction effects due to syneresis. Especially the gels prepared with the acid solution ($pH = 3.1$) showed a significant degree of radial contraction after aging. Because the gels are prone to breaking or cracking when exposed to air or any physical contact the dimensions were not checked rigorously. Instead, the diameter was measured for one or two rods per series. The diameter of the acid-catalyzed gels was found to be $10.40 ± 0.10$ mm after aging, whereas the diameter of the molds was $11.5 ± 0.1$ mm. The dimensions were measured with a digital caliper having an accuracy of $± 10$ µm. The diameter of the base-catalyzed gels reduced to $11.20 ± 0.10$ mm ($pH = 9.25$), respectively, $11.15 ± 0.10$ mm ($pH = 8.8$). The higher degree of shrinkage for the low $pH$ gels compared to the high $pH$ gels was also observed by Hdadch et al. [124] for similar gels. Although the length of the gel rods could not be checked, due to the type of molds used, it is assumed that...
The shrinkage occurred uniformly in all three dimensions. The volume contraction factor is therefore equal to \((d_{\text{final}}/d_{\text{initial}})^3\).

Relaxation analysis

The data obtained from the beam bending measurements was analyzed in terms of the applied load versus time. The normalized load of each measurement was plotted and fitted with Eq. 7.9 using the hydrodynamic relaxation expression for cylinders (Eq. 7.1) and the stretched exponential function (Eq. 7.10) for the viscoelastic contribution. The measured relaxation and the fit were in excellent agreement for each gel rod. Figure 7.3 shows the results for one of the gel rods \((\phi_{\text{Si}} = 0.123 \pm 0.007, \text{pH} = 3.1, \text{no extra salt added, aging time 91 hours})\). It can be observed in this figure that the gel exhibits a significant degree of VE relaxation, but the effect is only important on a time scale much longer than the time scale of the hydrodynamic relaxation and both relaxation effects are well separated. Similar VE behavior was exhibited by all other gel rods. The VE relaxation is attributed to the presence of water in the pores, and chemical attack of the water on the present siloxane bonds in the network [126, 135]. Therefore, the exchange of the mother liquid with ethanol appears to be incomplete, nevertheless the hydrodynamic relaxation could readily be extracted from the relaxation data.

For the gels the fit yields the following parameters. First, Poisson’s ratio \(\nu_p\) was directly calculated from the amount of hydrodynamic relaxation \(A\) resulting from the fit. The average \(\nu_p\) was found to be 0.20 ± 0.02. The modulus \(E_p\) follows from \(A\) and
the initial load $W_0$. The bulk shear modulus $G_p$ is subsequently derived from $E_p$ using Poisson’s ratio. The fit also yields $\tau_R$ from which the permeability $D$ is calculated using Eq. 7.2. The viscosity $\eta_L$ of ethanol is about 1.07 mPa s at room temperature [67]. The measured moduli and permeabilities for the gel rods are listed in Table 7.1 and are further discussed below.

### Acid-catalyzed gels

In series I ($pH = 3.1$, total reaction and aging time of 43 hours, and with varying $\phi_{Si}$) the modulus $E_p$ increases from $5.9 \pm 0.2$ MPa for the lowest (approximate) silica fraction, $\phi_{Si} = 0.113 \pm 0.007$, to $22.8 \pm 0.9$ MPa for the highest fraction, $\phi_{Si} = 0.149 \pm 0.009$. The gels of series II were cured and aged for 91 hours and contain a varying amount of additional sodium-chloride. The modulus of the first gel with $C_S = 0$ is $18.6 \pm 0.7$ MPa, which is high compared to the moduli of the gels in series I. Due to aging the silica network becomes more consolidated leading to enhanced elastic moduli. Addition of sodium-chloride to the gelling solution resulted in lower values of $E_p$ of about $15.5$ MPa but with no clear correlation to $C_S$ within the range considered. According to Martin and Odinek [136] the presence of small amounts of salt has little influence on the structure and growth of acid-catalyzed silica alcogels. The little variation of $E_p$ for series II is in agreement with this finding, though the difference in $E_p$ between the gel without extra salt ($E_p$ is about 20% higher) and the gels with extra salt cannot be explained at this point.

The permeability $D$ of the acid-catalyzed gels is on the order of $1$ nm$^2$. In series I the permeability decreases from $1.04 \pm 0.06$ nm$^2$ for the lowest silica fraction to $0.38 \pm 0.02$ nm$^2$ for the highest fraction. The average permeability of the gels in series II is $0.72 \pm 0.04$ nm$^2$, which corresponds well with the permeability results of series I, given the silica fractions $\phi_{Si}$. The additional salt slightly increases the permeability, but this is not a clear function of concentration.

### Base-catalyzed gels

In series IV ($pH = 8.8$, total reaction and aging time of 72 hours, and varying $\phi_{Si}$) the modulus $E_p$ increases from $1.4 \pm 0.1$ MPa for the lowest silica fraction, $\phi_{Si} = 0.078 \pm 0.004$, to $4.0 \pm 0.2$ MPa for the highest fraction, $\phi_{Si} = 0.100 \pm 0.005$. The moduli of the gels in series III ($pH = 9.25$) have an average value of $7.1 \pm 0.3$ MPa and appear to be independent of $C_S$ within the range considered. The average modulus is high with respect to the moduli of the gels in the other series, given the approximate silica densities $\phi_{Si}$. The faster gelation of the sol-gel solutions in series III compared to the gels in series IV implies that the effective aging time was longer for the gels in series III, so that higher values for $E_p$ are expected. In general, the modulus $E_p$ for the acid and base-catalyzed gels is a strong function of $\phi_{Si}$ and there is no significant difference in the order of magnitude of $E_p$ for both types of gels, given the different values of $\phi_{Si}$.

For the gels in series III the permeability increases from $14.8 \pm 0.7$ nm$^2$ for $C_S = 0$ mMolal to $26 \pm 2$ for $C_S = 60$ mMolal. Although the additional sodium-chloride did not affect $E_p$, the permeability is strongly affected when $C_S$ increases from 0 to 60 mMolal.
The permeability of the gels in series IV decreases from $40 \pm 2$ nm$^2$ for the lowest silica fraction to $20 \pm 1$ nm$^2$ for the highest silica fraction.

The base-catalyzed gels exhibit permeabilities 10 to 100 times greater in magnitude than the permeabilities of the acid-catalyzed gel, which cannot be explained by the difference in approximate silica fraction. The higher permeability for the base-catalyzed gel is due to the different pore structure, i.e. during the sol-gel reaction the silica forms thicker branches and larger aggregates than in acid systems, resulting in bigger pores at a given total silica concentration. The permeability of silica gels can be estimated using a Carman-Kozeny type of equation, such as [125, 128]

$$D = \frac{(1 - \phi_{Si})r_w^2}{4\kappa_w(\phi_{Si})},$$  \hspace{1cm} (7.11)

where $r_w$ is the mean pore radius of the gel and $\kappa_w$ is the Kozeny constant. The latter can be approximated by [128]

$$\kappa_w(\phi) \approx 1.0 + 6.05\phi^{0.5} - 8.60\phi + 6.56\phi^{1.5}. \hspace{1cm} (7.12)$$

Given the solid fractions of the gels $\kappa_w$ varies between 2.16 and 2.43. The experimental values of $D$ against $\phi_{Si}$ for series I and IV can adequately be fitted with Eq. 7.11, yielding $r_w = 53 \pm 5$ nm for the base-catalyzed gels and $r_w = 8.9 \pm 0.4$ nm for the acid-catalyzed gels.

### 7.4.2 Sandstone slabs

**Beam bending of untreated sandstone**

The response of a few untreated sandstone beams upon bending was checked in order to determine the moduli and the degree of VE behavior. The first measurement consisted of a dynamic Young modulus test on a dry rock sample. An oscillating deflection, in the form of a sawtooth, was imposed on the sample with a frequency of 0.05 Hz and an amplitude of 10 µm, yielding $E_p = 11.3 \pm 0.2$ GPa. Subsequently, the rock was saturated with acid water ($pH = 3.1$) and $E_p$ dropped to $7.6 \pm 0.1$ GPa. Repeated measurements, performed over six days, yielded the same constant value of $7.5 \pm 0.1$ GPa.

A second dry, untreated rock sample was subjected to a constant deflection of about 35 µm during which the load was measured. The normalized load curve is shown in Figure 7.4. The modulus of the dry rock is $E_p = 11.2 \pm 0.2$ GPa. The normalized load gradually relaxed to about 0.87 within 17 hours. Next, the rock sample was saturated with demineralized water. Again, a bending experiment was conducted yielding a reduced modulus, i.e. $E_p = 6.9 \pm 0.1$ GPa, and a higher degree of relaxation (see Figure 7.4). Since the hydrodynamic relaxation, due to the flow of water in the gel-free pores, occurs within several microseconds (estimated using Eq. 7.8) the observed relaxation is due to VE effects, similarly to the case with the dry rock. Subsequently, the rock sample was dried again at 60 °C for 20 hours and a third cycle under dry conditions was performed. The modulus was partly restored, having a value of $9.7 \pm 0.2$ GPa. The degree of VE relaxation remained similar to that of the wet case. Finally, the bath was filled with
Fig. 7.4: Relaxation of normalized load on untreated sandstone in beam bending experiment. The condition of the rock sample is indicated in the legend. The absolute load varied among the different cycles. The solid curves indicate the fits with a stretched exponential.

Table 7.2: Results of fit on normalized load for untreated sandstone sample using a stretched exponential. The modulus $E_p$ is derived from the initial load.

<table>
<thead>
<tr>
<th>cycle</th>
<th>condition</th>
<th>$\tau_{VE}$ [10$^6$ s]</th>
<th>$\alpha$</th>
<th>$E_p$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dry</td>
<td>3700 $\pm$ 400</td>
<td>0.177 $\pm$ 0.001</td>
<td>11.2 $\pm$ 0.2</td>
</tr>
<tr>
<td>2</td>
<td>water-saturated</td>
<td>0.25 $\pm$ 0.01</td>
<td>0.304 $\pm$ 0.002</td>
<td>6.9 $\pm$ 0.1</td>
</tr>
<tr>
<td>3</td>
<td>re-dried (20 h at 60 °C)</td>
<td>1.3 $\pm$ 0.1</td>
<td>0.248 $\pm$ 0.003</td>
<td>9.7 $\pm$ 0.2</td>
</tr>
<tr>
<td>4</td>
<td>ethanol-saturated</td>
<td>4.0 $\pm$ 0.3</td>
<td>0.238 $\pm$ 0.002</td>
<td>9.2 $\pm$ 0.1</td>
</tr>
</tbody>
</table>

ethanol and a fourth bending test was conducted. The modulus decreased to $9.2 \pm 0.1$ GPa. The degree of VE relaxation was comparable to that of the third cycle (see Figure 7.4). The relaxation curves were fitted to the stretched exponential function (see Figure 7.4). Table 7.2 contains the resulting fit parameters. A decreasing $\tau_{VE}$ and increasing $\alpha$ imply an increasing degree of VE relaxation within a fixed time interval.

**SEM and XRD analysis on untreated rock**

Similar VE behavior was observed in beam bending experiments on other types of sandstone by Jiménez González and Scherer [137]. The sandstones used were rich in clay and exhibited swelling behavior as they were saturated with water. The dilatometry tests on the Bentheim sandstone showed no change in length upon wetting the samples, thus the presence of swelling clays is negligible.

Several surface features were imaged and analyzed for chemical composition. A SEM
image of the surface obtained at a low magnification is given in Figure 7.5. The image clearly shows the coarse structure of the grains which are held together by siliceous cement. Though the SEM-EDX analysis is semi-quantitative at best a little amount of clay was found in local spots on the sample surface. The clay mainly consisted of silica and aluminum without other cations, and is therefore likely to be kaolinite. Contamination of the non-swelling clay due to cations introduced by the buffered solutions in the treated rock samples may enhance the swelling behavior. The XRD results only showed quartz, which indicates that the clay found in the SEM analysis was only present in small quantities. Despite the absence of swelling clays the grains appear to slip when a load is applied on the rock sample. The presence of water significantly reduces the elastic modulus of the rock and leads to an enhanced degree of VE relaxation with respect to a dry rock.

Beam bending of treated sandstone

The experimental results obtained for two series of treated sandstone are discussed in this section. The rock samples in series A were treated with acid-catalyzed gel, whereas the rock samples in series B were treated with base-catalyzed gel. The TMOS concentration was varied in both series, but no additional sodium-chloride was added to the gelling solutions. The properties of the treated rock samples are listed in Table 7.3. The total reaction and aging time was 72 hours for all rock samples. Glycerol from fresh and tightly sealed bottles was used in the bath and for the exchange with the original pore liquid. Exposure to air was avoided as much as possible for the glycerol in the exchange bath. Therefore it is assumed that the glycerol in the samples is free of water, so that the viscosity at 26 °C is ≃ 0.870 Pa s [138]. The bulk modulus $K_L$ is 4.80 GPa [138]. The normalized load curves for series A and B are shown in Figure 7.6 and Figure 7.7, respectively. The total measurement time for each curve is about one hour. Two experiments in series A were extended to more than 10 hours. All load curves show a monotonic decrease within the times of measurement and none of the load curves reaches a plateau. The overall decrease in magnitude of the normalized load varies but appears to increase
### Table 7.3: Properties of the treated sandstone samples

φ<sub>Si</sub> is the estimated volume fraction of silica assuming full hydrolysis and condensation, without correction for shrinkage. The thickness of the plates is given by 2a. The superscript b is used to indicate the duplicate samples prepared with the same gelling solutions as the complementary samples (see Section 7.3.2). The uncertainties in <i>E</i><sub>p</sub>, <i>D</i> and <i>A</i> are based on the quality of the fits.

<table>
<thead>
<tr>
<th>series</th>
<th>φ&lt;sub&gt;Si&lt;/sub&gt;</th>
<th>pH</th>
<th>2a [± 0.05 mm]</th>
<th>&lt;i&gt;E&lt;/i&gt;&lt;sub&gt;p&lt;/sub&gt; [GPa]</th>
<th>&lt;i&gt;D&lt;/i&gt; [nm&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>&lt;i&gt;A&lt;/i&gt; [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.071</td>
<td>3.1</td>
<td>10.00</td>
<td>9.3 ± 0.3</td>
<td>59 ± 7</td>
<td>0.049 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>0.071&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.1</td>
<td>9.80</td>
<td>8.5 ± 0.1</td>
<td>95 ± 13</td>
<td>0.047 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>0.084</td>
<td>3.1</td>
<td>8.92</td>
<td>11.3 ± 0.5</td>
<td>112 ± 15</td>
<td>0.110 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>0.084&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.1</td>
<td>8.05</td>
<td>10.1 ± 0.1</td>
<td>20 ± 2</td>
<td>0.097 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>0.097</td>
<td>3.1</td>
<td>9.40</td>
<td>11.6 ± 0.2</td>
<td>8 ± 1</td>
<td>0.166 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>0.097&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.1</td>
<td>9.70</td>
<td>10.6 ± 0.2</td>
<td>91 ± 12</td>
<td>0.160 ± 0.005</td>
</tr>
<tr>
<td>B</td>
<td>0.071</td>
<td>8.8</td>
<td>10.00</td>
<td>14.8 ± 0.1</td>
<td>94 ± 9</td>
<td>0.044 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>0.071&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.8</td>
<td>9.70</td>
<td>14.4 ± 0.1</td>
<td>56 ± 5</td>
<td>0.042 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>0.084</td>
<td>8.8</td>
<td>9.42</td>
<td>15.4 ± 0.2</td>
<td>52 ± 4</td>
<td>0.071 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>0.097</td>
<td>8.8</td>
<td>8.90</td>
<td>10.7 ± 0.3</td>
<td>14 ± 1</td>
<td>0.226 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>0.097&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.8</td>
<td>10.10</td>
<td>11.1 ± 0.2</td>
<td>50 ± 4</td>
<td>0.153 ± 0.003</td>
</tr>
</tbody>
</table>

with increasing (estimated) φ<sub>Si</sub>. The total amount of hydrodynamic relaxation <i>A</i>, which is independent of the permeability, can be approximated using Eq. 7.7. Poisson’s ratio is unknown, but we used \( \nu_p = 0.25 \), which is a good estimate for sedimentary rocks [139]. The elastic modulus <i>E</i><sub>p</sub> is about 10 GPa, so that \( K_p = 6.7 \) GPa. The solid fraction is \( \rho \approx 0.8 \), and therefore \( K_S \approx 10.5 \) GPa. Calculation of \( A \) then yields a value of 0.04.

Using the estimated maximum of \( A \) and the measured initial load values, the moduli of the treated samples were determined. The results are listed in Table 7.3. The samples in series A have an average modulus of 10 ± 1 GPa. Three of the samples in series B show a higher modulus of about 15 GPa, whereas the other two have a modulus of about 11 GPa. Compared to moduli of the untreated rock samples the moduli are at least as high and in some cases almost 50 % higher with respect to the dry rock. However, the treated rock samples contain a gelled solution. Though the presence of a liquid, especially water, would soften the rock, the relatively high moduli, extracted from the initial load values, indicate that the gel reinforces the structure. The high degree of VE relaxation observed in most of the relaxation curves is attributed to inelastic behavior of the combined sandstone-gel system upon deflection. The apparent correlation between increasing silica fraction φ<sub>Si</sub> and the overall magnitude of relaxation may be explained by two mechanisms.

First of all, the correlation suggests that the reinforcement effect of the gel becomes weaker with increasing φ<sub>Si</sub>. Presumably, the gel is more susceptible to syneresis and loss of adhesion during bending of the sample when φ<sub>Si</sub> is high [24]. The effective modulus would decrease rapidly and result in an apparent strong VE behavior. Secondly, there could be a thin layer of gel on the upper surface of the sample, lying between the pushrod...
7. Permeability reduction in porous materials by in situ formed silica gel

Fig. 7.6: Normalized load measured in beam bending experiments on gel treated sandstone samples (series A, acid-catalyzed gel). The estimated silica fraction of the gels is given in the legend. The superscript $b$ is used to indicate the duplicate samples prepared with the same gelling solutions as the complementary samples. The solid curves represent the fits using the combined hydrodynamic and VE relaxation function.

Fig. 7.7: Normalized load measured in beam bending experiments on gel treated sandstone samples (series B, base-catalyzed gel). The estimated silica fraction of the gels is given in the legend. The superscript $b$ is used to indicate the duplicate samples prepared with the same gelling solutions as the complementary samples. The solid curves represent the fits using the combined hydrodynamic and VE relaxation function.
7.4. Results and discussion

and the rock sample, that is crushed during bending, leading to a decrease in deflection of the sample and relaxation of the load. In case the gel layer is weak and compliant with respect to the rock then the pre-loading method applied in the experiments should prevent this problem. The high loads obtained in the experiments also suggest that the load is not borne by a weak gel layer. However, if the layer is dense and has a modulus similar to the rock the pushrod would still effectively bend the rock sample and produce the high loads. Since the gel layer is thin, it would not directly contribute to the total stress, hence load, in terms of the elastic and hydrodynamic effects. Still, the fast relaxation of the load may be due to a fast deformation of the gel layer in contact with the pushrod and the supports, resulting in a decreasing strain in the rock sample. The effect of this apparent slip mechanism or real slip at the surface is analyzed theoretically in Appendix C.

In the ideal situation the gel would completely fill the pore space of the rock. The overall permeability of the rock sample would be equal to or smaller than the intrinsic permeability of the gel. To a first-order approximation the permeability would equal the intrinsic permeability of the gel times the porosity (about 0.2) of the rock. Ideally, upon bending the hydrodynamic relaxation would be described by Eq. 7.4 with an $A$ value of about 0.04. Given the intrinsic permeability of the gels, the corresponding relaxation time $\tau_R$ would be about $1 \times 10^4$ s for the rock samples treated with acid-catalyzed gel (series A) and $\tau_R$ would be about $1 \times 10^3$ s for the rock samples treated with base-catalyzed gel (series B). The inflection point, demarcating the final plateau of $R$, is found at $t \approx 0.2\tau_R$.

The relaxation data of the rock samples in series B (see Figure 7.7) show a clear inflection point between 10 and 100 seconds. Despite the high degree of relaxation at the inflection points for the samples with $\phi_{Si} = 0.084$ or $\phi_{Si} = 0.097$, the relaxation curves were successfully fitted with the common expressions for hydrodynamic and VE relaxation (Eqs. 7.4 and 7.10), which is demonstrated in Figure 7.7. The extracted parameters $D$ and $A$ are given in Table 7.3. For the two samples with $\phi_{Si} = 0.071$ the curve fit was adequate yielding values for $A$ of about 0.05, and a permeability of 59 $\pm$ 7 nm$^2$, respectively, 95 $\pm$ 13 nm$^2$. For the higher concentration samples the fit of the relaxation curves was less accurate. As can be observed in Figure 7.6 the inflection points in the fitted curves do not agree well with the inflection points in the measured load curves. The extracted permeability for these samples ranges between 8 and 112 nm$^2$, but these values can only indicate the order of magnitude. Compared to the intrinsic permeability of the acid-catalyzed gel rods the overall permeability of the rock samples is higher. However, at a given TMOS concentration the gel rods exhibited a high degree of
contraction and pore size reduction. The order of magnitude of the permeability found in series B is comparable to the values found in series A.

7.5 Conclusion

The intrinsic permeability and elastic modulus of various TMOS-based silica alcogels were successfully measured with the method of beam bending. Addition of sodium-chloride, up to 80 mMolal, and the pH of the solution had no significant effect on the modulus, whereas increasing curing and aging times resulted in increased moduli. The permeabilities decreased with increasing silica fraction and aging time. The permeability of the acid-catalyzed gels was on the order of 1 nm$^2$. The base-catalyzed gels yielded permeabilities 10 to 100 times higher in magnitude than the acid-catalyzed gels, which is not exclusively attributed to the lower silica fractions of the acid-catalyzed gels, but also to the difference in pore structure of the network. Untreated Bentheim sandstone exhibits a significant viscoelastic behavior upon bending, which is due to slip between the grains and the low amount of siliceous cement. The permeability of rock samples treated with base-catalyzed gel is on the order of 10 to 100 nm$^2$ without a clear correlation to the silica density of the gel, and is at least as high as the intrinsic permeability of the corresponding gel samples. The permeability of the rock samples treated with acid-catalyzed gel was determined less accurately, but is on the same order of magnitude as for the alkaline series. The findings imply that the gel is not uniformly distributed in the pore space, and that the effectiveness of the treatment varies between the samples, but is insensitive to the pH and concentration of the gelling solution. Compared to the untreated rock the overall permeability is reduced by a factor of at least $10^4$, so that the gel adequately blocks the pores.
A physical-mathematical model was developed to describe the injection and reactive transport of an oil-soluble chemical (OSC) under two-phase conditions in a porous medium. The model follows from the classical mass balance equations for two-phase flow and includes the mass fractions for each component and the mass transfer and reaction terms. Numerical calculations were performed to investigate the effect of the parameters (flow rate, reaction rate, etc.) on the mass transfer behavior and concentration profiles. The model was used to simulate the core flow experiments (see Chapter 6), but can also be used to simulate the injection of an OSC in an idealized reservoir, assuming linear flow.

8.1 Introduction

It was found in the bulk phase experiments (see Chapters 2, 3 and 4) and in the core injection experiments (see Chapter 6) that the mass transfer of TMOS is predominantly driven by the hydrolysis reaction of TMOS in the aqueous phase. An important aspect is the solubility of TMOS in water, which is initially poor [24, 34], but the solubility is increased by the formation of methanol due to the hydrolysis reaction. The rate of hydrolysis is a strong function of pH, i.e. the rate is minimum at neutral conditions, but it increases in the presence of acid- or base-catalysts. Further, the reaction rates, hence the mass transfer rates, increase with temperature. In bulk the mass transfer occurs typically on a time scale of hours. The mass transfer in the porous materials is complete on a time scale of less than one hour up to many hours, depending on pH and temperature.

The number of existing models for the simulation of reactive transport of an oil-soluble chemical in porous media is limited. A network model was presented by Thompson and Fogler [42] to simulate the injection of TMOS in a porous medium. Their work was focussed on the displacement behavior on the pore scale and the effect of changing viscosity of the aqueous phase due to the gel reaction. Recently, Valiollahi developed a model to simulate the placement of TMOS in sandstone based on classical two-phase flow equations [140].

The physical-mathematical model presented in this chapter simulates the reactive transport of TMOS/oil in porous media under two-phase conditions. The model assumes linear flow and can be used to simulate the injection of an OSC in a simple reservoir. As such it can be employed in the design process of a water shut-off treatment in order to predict pressure profiles, gel distribution profiles, etc.
In this chapter the problem is considered for a homogeneous, water-wet cylinder (core) and is described in one dimension. The core is initially saturated with pure oil and pure water at irreducible water conditions. Two cases were considered; first of all the injection of a limited amount (or batch) of TMOS-oil solution followed by a shut-in of the system (i.e. no injection of fluids). This case represents the conditions in the core injection experiments described in Chapter 6. The obtained mass transfer profiles are compared with the experimental profiles. In the second case the solution is injected continuously throughout the simulation interval. This case is of interest when a large amount of solution is placed and/or a low injection rate is employed. In both cases the condensation reaction of the hydrolyzed molecules is neglected. The effect of condensation is, however, assessed qualitatively in one set of simulations by varying the aqueous phase viscosity. The effect of solubility was included in the model through the use of a partitioning equation. A simple capillary bundle model was used to describe the pore-scale diffusion of TMOS between both phases considering the equilibrium concentrations. The effect of main parameters, such as flow rate and amount of mixture injected, on the concentration and saturation profiles was investigated. In addition, the differential pressure over the core was calculated for the case of continuous injection.

\[
Q \quad S_w(z,t) \quad P_{out}
\]

\[z=-L/2 \quad z=L/2\]

**Fig. 8.1:** Schematic view of porous system (core) in the model. The core has a length \(L\), cross-section \(A\), porosity \(\varphi\) and absolute permeability \(K_{abs}\). The fluids are injected at the inlet \((z = -L/2)\) with a flux \(Q\). In this example the water saturation \((S_w)\) profile represents a drainage process. The outlet pressure at \(z = L/2\) is equal to \(P_{out}\).

### 8.2 Theoretical background

#### 8.2.1 Problem statement

Consider a homogeneous porous cylinder (core) with a length \(L\) and cross-section \(A\) (see Figure 8.1). The core has a uniform porosity \(\varphi\) and uniform absolute permeability \(K_{abs}\). In the following the problem is described in one dimension, and \(z\) represents the spatial coordinate along the length of the core. The water saturation is given by \(S_w(z, t)\) and, hence, the oil saturation \(S_o\) is equal to \(1 - S_w\). The composition of each phase is defined by the mass fraction \(w_X^\alpha(z, t)\), where \(\alpha\) represents the phase \((w = \text{aqueous phase and } o = \text{oleic phase})\) and \(X\) indicates the component \((O = \text{oil}, W = \text{water}, T = \text{TMOS}, M = \text{methanol}, \text{and } SA = \text{silicic acid})\). The mass fractions are defined such that \(\sum_X w_X^\alpha = 1\). In the oleic phase only TMOS and oil exist, and in the aqueous phase only water, TMOS, methanol and silicic acid exist.
A mixture of TMOS/oil, with a fraction \( w_o^T = w_0 \), is injected with an injection rate \( Q \) at the inlet of the core, which is found at \( z = -L/2 \), and subsequently fluids are produced at the outlet which is found at \( z = L/2 \). As the TMOS comes in contact with water, the TMOS partitions between both phases. In the aqueous phase the TMOS reacts with water. The reaction products are silicic acid and methanol. The condensation of silicic acid is neglected. The effect of gravity is also neglected.

### 8.2.2 Material balance equation

The reactive transport can be described by the following material balance equation (with respect to each species \( X \) and phase \( \alpha \)):

\[
\varphi \frac{\partial \left( \rho_\alpha s_\alpha w_\alpha^X \right)}{\partial t} = \frac{\partial}{\partial z} \left( \lambda_\alpha \frac{\partial P_\alpha}{\partial z} \rho_\alpha w_\alpha^X \right) + U_\alpha^X + \varphi s_\alpha R_\alpha^X ,
\]

where \( \rho_\alpha, \lambda_\alpha, P_\alpha, U_\alpha^X \) and \( R_\alpha^X \) are the density, the mobility, the pressure, the flux of TMOS, and the reaction terms of phase \( \alpha \), respectively. The mobilities \( \lambda_\alpha \) are given by

\[
\lambda_\alpha = \frac{K_{abs} k_{ra}}{\mu_\alpha} ,
\]

where \( k_{ra} \) is the relative permeability, and \( \mu_\alpha \) the viscosity of phase \( \alpha \). The relative permeabilities \( k_{rw} \) and \( k_{ro} \) are modeled using the Brooks-Corey relations [141], given by

\[
k_{rw} = k'_{rw} \left( S_{we} \right)^{2+3\zeta},
\]

respectively,

\[
k_{ro} = k'_{ro} \left( 1 - S_{we} \right)^2 \left[ 1 - \left( S_{we} \right)^{2+\zeta} \right].
\]

Here \( \zeta \) is a sorting factor and the effective saturation \( S_{we} \) is defined as

\[
S_{we} = \left( \frac{S_w - S_{wi}}{1 - S_{wi} - S_{or}} \right),
\]

where \( S_{or} \) is the residual oil saturation, and \( S_{wi} \) is the irreducible (or residual) water saturation.

The viscosity of the oleic phase, \( \mu_o \), is a function of the TMOS fraction. Here we use the Grunberg-Nissan relation to calculate the viscosity, which is given by [61]

\[
\log \mu_o = x \log \mu^T + (1 - x) \log \mu^O ,
\]

where \( x \) is the mole fraction of TMOS in oil, and \( \mu^T \) and \( \mu^O \) are the viscosities of pure TMOS and pure oil, respectively. In absence of a condensation reaction, the viscosity of the aqueous phase remains constant.

The pressure in the oleic phase, \( P_o \), is related to the pressure in the aqueous phase, \( P_w \), by

\[
P_c = P_o - P_w ,
\]
where $P_c$ is the capillary pressure, which can be modeled using a Leverett-$J$ function [118]. For a water-wet medium the function is given by

$$P_c = \frac{\sigma}{2} \sqrt{\frac{\varphi}{K_{abs}}} \left( \frac{0.5 - S_{wi}}{1 - S_{wi} - S_{or}} \right)^{1/\xi} \left( \frac{S_w - S_{wi}}{1 - S_{wi} - S_{or}} \right)^{-1/\xi},$$

where $\sigma$ is the interfacial tension (IFT), and $\xi$ is a sorting factor.

Fig. 8.2: Schematic view of the capillary bundle system which is used as an upscaling model for the pore-scale mass transfer of TMOS. The tube radius is defined as $r_w$.

### 8.2.3 Initial and boundary conditions

Initially the core is homogeneously saturated at the irreducible water saturation $S_{wi}$. The aqueous phase only consists of water and the oleic phase only consists of oil. The pressure in the oleic phase is atmospheric. Therefore the initial conditions are

$$P_o(z,0) = 1 \quad ; \quad S_w(z,0) = S_{wi} \quad ; \quad w^T_o(z,0) = 0 \quad ; \quad w^W_w(z,0) = 1. \quad (8.9)$$

For $t > 0$, the pressures $P_\alpha$ are governed by the injection rate $Q$, the outlet pressure $P_{out}$ and the capillary pressure $P_c$. The outlet pressure $P_{out}$ is equal to the atmospheric pressure, and the capillary pressure at the outlet is zero. The injection of the mixture stops at $t = t_s$ (i.e. the shut-in period of the core starts when the injection stops). The boundary conditions are therefore given by

$$w^T_o(-L/2,t) = w_0 \quad t > 0, \quad (8.10)$$

$$Q = -A\lambda_o \frac{\partial P_o(-L/2,t)}{\partial z} \quad 0 > t > t_s, \quad (8.11)$$

$$\frac{\partial P_o(-L/2,t)}{\partial z} = 0 \quad t > t_s, \quad (8.12)$$

$$P_o(L/2,t) = P_w(L/2,t) = P_{out} \quad t > 0. \quad (8.13)$$

### 8.2.4 Mass transfer

The flux term $U_X^\alpha$ is non-zero only for $X = T$ (i.e. for TMOS). In order to describe the mass transfer of TMOS between both phases an up-scaling model is needed which links the microscopic mass transfer (on the pore scale) with the macroscopic transport model. The geometry of the pore space in the stone is complex and difficult to include in the model. Therefore we adopt a simplified geometry in the form of a capillary bundle system
(see Figure 8.2). As opposed to the bulk mass transfer model (see Chapters 3 and 4) we include a diffusion term in the mass transfer term $U^T_o = -U^T_w$, which can be readily incorporated in the two-phase flow model. The term $U^T_o$ follows from a description of simple diffusion between both phases within the capillary bundle system, and is given by

$$U^T_o = -\frac{4D\varphi}{r_w^2\left(1 + S_o^{-1/2}\right)}\left(\hat{\rho}_o - \hat{\rho}_o^{eq}\right), \quad (8.14)$$

where $D$ is an effective diffusion coefficient, $r_w$ is the average pore radius, and $\hat{\rho}_o$ is the density of TMOS in the oleic phase, which is equal to $\rho_o w^T_o$. The equilibrium coefficient $\hat{\rho}_o^{eq}$ follows from the partitioning function

$$\hat{\rho}_o^{eq} = \hat{\rho}_w^{eq}\exp\left(\frac{\varepsilon}{R_g T}\right), \quad (8.15)$$

and the total density of TMOS $\hat{\rho}^T$, given by

$$\hat{\rho}^T = \hat{\rho}_o + \hat{\rho}_w. \quad (8.16)$$

In Eq. 8.15 $R_g$ is the gas constant, $T$ is the temperature, and $\hat{\rho}_w$ is equal to $\rho_w w^T_w$. The interaction parameter $\varepsilon$ is a function of the methanol concentration in water. Due to the poor solubility of TMOS in water the interaction parameter is on the order of $R_g T$ but decreases as the concentration of methanol is increased due to the hydrolysis of TMOS in water. As a first order approximation, the parameter $\varepsilon$ is chosen as (see also Chapter 3)

$$\varepsilon = \varepsilon_0 \left(1 - a w^M_w\right), \quad (8.17)$$

where $\varepsilon_0$ is the interaction parameter in absence of methanol and $a$ is an arbitrary scale factor greater than zero.

### 8.2.5 Reaction terms

In case of full hydrolysis a TMOS molecule reacts with water according to

$$\text{Si(OCH}_3\text{)}_4 + \text{4H}_2\text{O} \rightarrow \text{Si(OH)}_4 + \text{4CH}_3\text{OH}. \quad (8.18)$$

The reaction terms $R^X_\alpha$ only exist for the aqueous phase, $\alpha = w$, and are related to a single molar reaction term $R$ by

$$R^T_w = -M^T R; \quad R^W_w = -4M^W R; \quad R^{SA}_w = M^T R; \quad R^M_w = 4M^T R, \quad (8.19)$$

where $M^X$ is the molar weight of species $X$. The molar reaction term is given by

$$R = k_h^t \left(C^T_w\right)^\beta \left(C^w_w\right)^\gamma$$

$$= \frac{k_h^t}{(M^T)^\beta (M^W)^\gamma} \left(C^T_w\right)^\beta \left(C^w_w\right)^\gamma$$

$$= k_h \left(C^T_w\right)^\beta \left(C^w_w\right)^\gamma$$

$$= k_h \left(\rho_w\right)^{\beta + \gamma \left(w^T_w\right)^\beta \left(w^w_w\right)^\gamma}, \quad (8.20)$$
where $C'$ [mol m$^{-3}$] and $C$ [kg m$^{-3}$] are the molar and mass concentration, respectively. Further, $k'_h$ and $k_h$ are the corresponding hydrolysis rate constants, and $\beta$ and $\gamma$ are reaction order coefficients. For a higher-order reaction term (i.e. $\beta + \gamma > 1$) the hydrolysis constant $k'_h$ is scaled inconveniently. A scale factor $Z$ is introduced such that $k'_h$ can be related to a first-order reaction rate $k$ [s$^{-1}$], i.e.

$$k'_h = Zk,$$  \hspace{1cm} (8.21)

where $Z [(m^3 \text{ mol}^{-1})^{\beta+\gamma-1}]$ can be expressed in terms of the molar volume of TMOS $V^T$ and the molar volume of water $V^W$. In our model we choose

$$Z = (V^T)^\beta (V^W)^{\gamma-1}. \hspace{1cm} (8.22)$$

### 8.3 Method of solution

#### 8.3.1 General equation

The equations are solved based on the IMPES method [142]. First the mass balance equations are rewritten in terms of the oil pressure using appropriate assumptions and relations. Subsequently, the equations are discretized. In the IMPES method first the pressure is solved for implicitly, after which the saturation (e.g. $S_o$) is solved for explicitly. In our extended model the mass fractions of the components are calculated implicitly, and the mass transfer and reaction terms are updated each time step [140].

Summation of the material balance equation for each component, given by Eq. 8.1, and applying the closure conditions result in the following material balance equations for the oleic phase and the aqueous phase, respectively:

$$\varphi S_o \frac{\partial \rho_o}{\partial t} = \varphi S_o \frac{\partial \rho_o}{\partial t} + \varphi \rho_o \frac{\partial S_o}{\partial t} = \frac{\partial}{\partial z} \left( \rho_o \lambda_o \frac{\partial P_o}{\partial z} \right) + U_o^T, \hspace{1cm} (8.23)$$

$$\varphi S_w \frac{\partial \rho_w}{\partial t} + \varphi \rho_w \frac{\partial S_w}{\partial t} = \frac{\partial}{\partial z} \left( \rho_w \lambda_w \frac{\partial P_w}{\partial z} \right) + U_w^T. \hspace{1cm} (8.24)$$

Expanding the left-hand side of Eqs. 8.23 and 8.24 yields

$$\varphi S_o \frac{\partial \rho_o}{\partial t} = \frac{\partial}{\partial z} \left( \rho_o \lambda_o \frac{\partial P_o}{\partial z} \right) + U_o^T, \hspace{1cm} (8.25)$$

and

$$\varphi S_w \frac{\partial \rho_w}{\partial t} = \frac{\partial}{\partial z} \left( \rho_w \lambda_w \frac{\partial P_w}{\partial z} \right) + U_w^T. \hspace{1cm} (8.26)$$

Dividing Eq. 8.25 by $\rho_o$, and dividing Eq. 8.26 by $\rho_w$, and adding both resulting equations yields

$$\frac{\varphi S_o}{\rho_o} \frac{\partial \rho_o}{\partial t} + \frac{\varphi S_w}{\rho_w} \frac{\partial \rho_w}{\partial t} = \frac{1}{\rho_o} \frac{\partial}{\partial z} \left( \rho_o \lambda_o \frac{\partial P_o}{\partial z} \right) + \frac{1}{\rho_w} \frac{\partial}{\partial z} \left( \rho_w \lambda_w \frac{\partial P_w}{\partial z} \right) + \left( \frac{1}{\rho_w} - \frac{1}{\rho_o} \right) U_w^T. \hspace{1cm} (8.27)$$
The densities $\rho_o$ and $\rho_w$ are functions of pressure and composition of the corresponding phases. Under isobaric conditions the density of phase $\alpha$ is given by

\[
\frac{1}{\rho_\alpha} = \sum_X \frac{w^X_\alpha}{\varrho^X},
\]

where $\varrho^X$ is the density of component $X$ in a pure liquid. The derivatives of the densities with respect to time can be approximated by (see Appendix D)

\[
\frac{\partial \rho_o}{\partial t} = \sum_{I \in \{O,T\}} \varrho^I \frac{\partial w^I_o}{\partial t} + c_o \rho_o \frac{\partial P_o}{\partial t},
\]

and

\[
\frac{\partial \rho_w}{\partial t} = \sum_{J \in \{W,T,M,SA\}} \varrho^J \frac{\partial w^J_w}{\partial t} + c_w \rho_w \frac{\partial P_w}{\partial t},
\]

where $c_o$ and $c_w$ are the average compressibility coefficients of the oleic and the aqueous phase, respectively. For the sake of simplicity the coefficients are assumed to be independent of composition. Substitution of Eqs. 8.29 and 8.30 in Eq. 8.27 and some rearrangements result in the following equation (with the assumption that $\partial P_c/\partial t \approx 0$)

\[
\varphi \left(S_o c_o + S_w c_w \right) \frac{\partial P_a}{\partial t} - \frac{1}{\rho_a} \frac{\partial}{\partial z} \left( \rho_o \lambda_o \frac{\partial P_o}{\partial z} \right) - \frac{1}{\rho_w} \frac{\partial}{\partial z} \left( \rho_w \lambda_w \frac{\partial P_a}{\partial z} \right) \\
= -\varphi \frac{S_o}{\rho_o} \sum I \varrho^I \frac{\partial w^I_o}{\partial t} - \varphi \frac{S_w}{\rho_w} \sum J \varrho^J \frac{\partial w^J_w}{\partial t} + \frac{1}{\rho_w} - \frac{1}{\rho_a} U_T^T - \frac{1}{\rho_w} \frac{\partial}{\partial z} \left( \rho_w \lambda_w \frac{\partial P_c}{\partial z} \right).
\]

### 8.3.2 Numerical solution

A one-dimensional grid is defined with $N$ grid blocks of size $\Delta z$. The mobility parameter and phase density are weighed upstream. The time step of integration is given by $\Delta t$. Details about the numerical solution are given in Appendix E. In short, the oil pressure is solved first, after which the oil saturation is updated explicitly. Subsequently, the mass fractions are updated implicitly. As the saturations, densities and fractions are updated the reaction rate $R$ can be calculated. The mass transfer term $U$ follows from the evaluation of the partitioning function (Eq. 8.15) and the total TMOS density (Eq. 8.16).

### 8.4 Results and discussion

#### 8.4.1 Choice of parameters

In this section the common parameters which have been used in the numerical calculations are defined first. The choice of the parameters is based on the conditions found in the
Table 8.1: Common parameters used in the simulations. The parameters are based on the conditions found in the core injection experiments, described in Chapter 6. Further details are given in Section 8.4.1.

<table>
<thead>
<tr>
<th>parameter</th>
<th>description</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{abs}$</td>
<td>absolute permeability</td>
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<td>$\mu$m$^2$</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>porosity</td>
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<td>-</td>
</tr>
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<td>$L$</td>
<td>length</td>
<td>0.06</td>
<td>m</td>
</tr>
<tr>
<td>$A$</td>
<td>cross-section</td>
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</tr>
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<td>$r_w$</td>
<td>pore radius</td>
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<td>$\mu$m</td>
</tr>
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<td>$V_{pore}$</td>
<td>total pore volume</td>
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<td>ml</td>
</tr>
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<td>$P_{out}$</td>
<td>outlet pressure</td>
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<td>bar</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
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<td>°C</td>
</tr>
<tr>
<td>$R_g$</td>
<td>gas constant</td>
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<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$S_{wi}$</td>
<td>residual water saturation</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>$S_{or}$</td>
<td>residual oil saturation</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>$w_0$</td>
<td>TMOS fraction in mixture</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>$\xi$</td>
<td>sorting factor for $P_c$</td>
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<td>-</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>sorting factor for $k_{ra}$</td>
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<td>-</td>
</tr>
<tr>
<td>$k'_{rw}$</td>
<td>end point relative permeability water</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>$k'_{ro}$</td>
<td>end point relative permeability oil</td>
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<td>-</td>
</tr>
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<td>$\sigma$</td>
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</tr>
<tr>
<td>$\beta$</td>
<td>reaction order coefficient</td>
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<td>-</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>reaction order coefficient</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>$Z$</td>
<td>scaling factor for $k'_h$</td>
<td>8.84$\times10^{-19}$</td>
<td>mol$^4$ m$^{-12}$</td>
</tr>
<tr>
<td>$N$</td>
<td>number of grid blocks</td>
<td>50</td>
<td>-</td>
</tr>
</tbody>
</table>
8.4. Results and discussion

In particular, we mention the following parameters. The absolute permeability is 1.6 \( \mu m^2 \), and the porosity is 0.22. The core has a length of 60 mm and a diameter of 14 mm. In each case the temperature is 25 °C and the atmospheric pressure, and thus the outlet pressure, is 1 bar. The residual saturations are \( S_{wi} = S_{or} = 0.25 \). The core is initially always at residual water, and the phases initially consist of pure oil and pure water, respectively. It is noted that the water used in the experiments was heavy water, so that we choose a density \( \rho^W \) of 1,100 kg m\(^{-3}\). The IFT between pure oil and pure water is around 50 mN m\(^{-1}\) [92]. The introduction of TMOS in the oleic phase or the reaction of TMOS in the aqueous phase lowers the IFT significantly (see Chapter 3). We choose a constant IFT of \( \sigma = 20 \) mN m\(^{-1}\).

The pore radius \( r_w \) is an estimate for Bentheim sandstone, based on experimental validation (see Chapter 6). The sorting factors for \( P_c \) and \( k_{ra} \) and the end point relative permeabilities \( k'_{ra} \) are chosen arbitrary but are representative for a water-wet porous rock [118]. The exact reaction order of the hydrolysis reaction is unknown, and it is likely to be sensitive to concentrations and pH [24]. In this model we link the reaction order to the stoichiometry of the hydrolysis reaction (see Eq. 8.18), so that \( \beta = 1 \) and \( \gamma = 4 \). In the following we distinguish between two scenarios. Case A represents the set of simulations in which a few pore volumes of mixture are injected, followed by shut-in. This case is representative of the core injection experiments discussed in Chapter 6. Case B represents the set of simulations in which the mixture is continuously injected. The results discussed in the following sections show the sensitivity of the problem to main parameters, such as \( k \) and \( Q \).

### Table 8.2: Fluid properties used in the simulations.

The compressibility factors \( c_o \) and \( c_w \) represent the average compressibilities of the oleic and the aqueous phase, respectively. The values are based on the compressibilities of pure \( n \)-hexadecane and pure water, respectively.

<table>
<thead>
<tr>
<th>parameter</th>
<th>description</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho^O )</td>
<td>density of oil</td>
<td>820</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>( \rho^T )</td>
<td>density of TMOS</td>
<td>1,032</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>( \rho^W )</td>
<td>density of (heavy) water</td>
<td>1,100</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>( \rho^M )</td>
<td>density of methanol</td>
<td>791</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>( \rho^{SA} )</td>
<td>density of silicic acid (^a)</td>
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<td>kg m(^{-3})</td>
</tr>
<tr>
<td>( \mu^O )</td>
<td>viscosity of oil</td>
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<td>mPa s</td>
</tr>
<tr>
<td>( \mu^T )</td>
<td>viscosity of TMOS</td>
<td>0.63</td>
<td>mPa s</td>
</tr>
<tr>
<td>( \mu^W )</td>
<td>viscosity of aqueous phase</td>
<td>1</td>
<td>mPa s</td>
</tr>
<tr>
<td>( c_o )</td>
<td>compressibility of oleic phase</td>
<td>( 9 \times 10^{-10} )</td>
<td>Pa(^{-1})</td>
</tr>
<tr>
<td>( c_w )</td>
<td>compressibility of aqueous phase</td>
<td>( 5 \times 10^{-10} )</td>
<td>Pa(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\) Silicic acid does not exist in liquid form, however, in order to calculate the density of the aqueous phase an estimate is used based on the conservation of mass.
8.4.2 Case A. Batch injection: example

The results of two of the simulations for case A are discussed first. We consider the case of fast injection \((Q = 1 \text{ ml min}^{-1})\) versus slow injection \((Q = 0.02 \text{ ml min}^{-1})\). The amount of oil/TMOS mixture is two pore volumes (PV). The diffusion constant \(D\) is \(10^{-10} \text{ m}^2 \text{s}^{-1}\). The interaction parameter \(\varepsilon_0\) is equal to \(5 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}\) and \(a = 4\) (the latter is four times higher than the parameter \(\alpha\) used in the bulk model due to a different scaling in Eq. 8.17). The reaction constant \(k\) is based on the reaction constants determined in the bulk experiments (see Chapter 4), i.e. \(k = 0.323 \times 10^{-3} \text{ s}^{-1}\) (which corresponds to the experiment without buffer). The total simulation time is 20 hours.

The water saturation profiles are shown in Figure 8.3. As the TMOS solution is injected the TMOS starts to partition between the oleic and aqueous phase in which it reacts to form methanol and silicic acid. Due to the mass transfer the saturation \(S_w\) increases and \(S_o\) decreases. The amount of mixture exceeds \((1 - S_w) \times 1 \text{ PV}\) and during injection not all TMOS transfers instantly from the oleic to the aqueous phase. Therefore, some of the TMOS solution is produced at the outlet between \(t = 0\) and \(t = t_s\). Given a certain reaction constant \(k\) and amount of PV injected, the flow rate \(Q\) has a significant effect on the degree of change of the \(S_w\) profiles, as can be observed in Figure 8.3. In case the injection is relatively fast compared to the reaction rate, the injection of the mixture results in uniform \(S_w\) profiles which increase gradually in the course of time during shut-in up to \(S_w \approx 0.42\). However, in case the injection is relatively slow compared to the reaction rate, the \(S_w\) profiles during injection start to develop a non-uniform and almost front-like behavior towards the outlet. During shut-in the ongoing mass transfer of TMOS results in uniform \(S_w\) profiles after several hours. The final saturation is however much higher \((S_w \approx 0.48)\) compared to that in the fast injection case.

**Fig. 8.3:** Water saturation profiles in the example simulations of Case A. Two PV of TMOS/oil were injected between \(t = 0\) and \(t = t_s\). Initially, \(S_w = S_{wi}\). The time step between different solid curves is 0.8 hours. The dashed curve is the saturation profile at \(t = t_s\). The reaction constant is \(k = 0.323 \times 10^{-3} \text{ s}^{-1}\). (left) \(Q = 1 \text{ ml min}^{-1}\). (right) \(Q = 0.02 \text{ ml min}^{-1}\).

Of main interest is the amount of silicic acid which is formed, since this indicates
8.4. Results and discussion

Fig. 8.4: Profiles of the amount of formed silicic acid (SA). Two PV of TMOS/oil were injected between \( t = 0 \) and \( t = t_s \). The time step between different solid curves is 0.8 hours. The dashed curve is the saturation profile at \( t = t_s \). (left) \( Q = 1 \, \text{ml min}^{-1} \). (right) \( Q = 0.02 \, \text{ml min}^{-1} \).

The amount of gel that can be formed. The product of the \( w_{SA} \) and \( S_w \) represents this amount, and the profiles are shown in Figure 8.4. The fast placement of the batch results in a gradual and uniform increase in the course of time of the amount of SA from zero to about 0.105. The slow placement results in a slightly non-uniform distribution but a higher amount of silicic acid formed \((w_{SA} \times S_w \approx 0.125)\).

Fig. 8.5: Profiles of the partition term \( E \). Two PV of TMOS/oil were injected between \( t = 0 \) and \( t = t_s \). The time step between different solid curves is 0.8 hours. The dashed curve is the saturation profile at \( t = t_s \). (left) \( Q = 1 \, \text{ml min}^{-1} \). (right) \( Q = 0.02 \, \text{ml min}^{-1} \).

The effect of the methanol concentration on the partitioning of TMOS between both phases is illustrated by the profiles of the partitioning coefficient \( E = \exp(\varepsilon/R_g T) \), which are shown in Figure 8.5. It can be observed that initially \( E \) is much larger than one, so
that the TMOS tends to remain in the oleic phase. However, \( E \) decreases as the methanol concentration is increased. Ultimately, \( E \) is about 0.8. It is noted that the values for \( E \) depend on the choice of \( \varepsilon_0 \) and \( a \), both of which are arbitrary at this point. In the following section these parameters are varied and the results are discussed.

Finally, from the simulated profiles of \( w_T^O \) the volume fractions \( \phi_T \) of TMOS in oil – at five different positions (slices) along the core – were derived and plotted against time (indicated by the solid curves in Figure 8.6). The purpose is to compare, qualitatively, the calculated concentration profiles with the experimentally derived concentration profiles (see also Chapter 6). Direct quantitative comparison with the experimental profiles is not plausible due to a number of uncertain parameters and due to the uncertainty in the measured profiles.

The experiments performed at 25 °C are considered. For the simulations the reaction constants \( k \) are based on the values obtained from the bulk experiments (see Chapter 4). As was discussed in Chapter 6 the experimentally determined concentration profiles

![Fig. 8.6: Measured concentration profiles in the core injection experiments (see also Chapter 6) for the different slice positions indicated by the symbols. The solid curves are the simulated concentration profiles. The reaction constants \( k \) are displayed in the graphs and are based on the bulk experiment results. The other parameters are defined in Sections 8.4.1 and 8.4.2.](image-url)
show initial values $\phi_T < 0.20$, which is due to a combination of fast mass transfer and incomplete displacement of oil by the oil/TMOS mixture during injection. The latter effect also leads to the significant differences between the several slices. The plateaus of $\phi_T$ between 0.01 and 0.08 are due to incomplete transfer of TMOS between both phases or to the presence of hydrogen in the aqueous phase, which leads to apparently high values for $\phi_T$ (see Chapter 6).

The calculated profiles for the different slices are virtually identical and do not show the non-uniform behavior found in the experiments. The calculated profiles show a decreasing $\phi_T$ which starts around 0.20 and goes to zero. Considering the time scale at which $\phi_T$ decays we observe the following. For the unbuffered system (A03) and the acid-catalyzed system (A05) the calculated rate of decay of $\phi_T$ agrees well with that observed in the experimentally obtained profiles. However, for the neutrally buffered system (A07) and the base-catalyzed system (A09) the calculated profiles decay much slower than the experimentally obtained profiles. A modified and refined reaction term will likely improve the reactive transport model for these systems, but this is left for future studies.

Fig. 8.7: Calculated final values (at $t = 20$ hours) for the average water saturation $S_w$, amount of silicic acid $w^{SA}_w \times S_w$ and fraction of silicic acid $w^{SA}_w$. In the simulation the batch size was 2 PV. (left) variation of $k$ with $Q = 1$ ml min$^{-1}$. (right) variation of $Q$ with $k = 0.323 \times 10^{-3}$ s$^{-1}$

8.4.3 Case A. Batch injection: effect of main parameters

The effect of the parameters $k$, $Q$, $D$, $\varepsilon_0$, $a$ and the number of pore volumes injected on the mass transfer profiles and silicic acid formation was analyzed for the batch injection case. First of all, the reaction rate $k$ was varied over two orders of magnitude. The other parameters were equal to those specified in the example simulation (see previous section). The effect of $k$ on the final oil saturation (i.e. after 20 hours), averaged over the core, is shown in the left-hand graph of Figure 8.7. It can be observed that the final average $S_w$ increases with increasing $k$, which is due to the enhanced mass transfer rate with increasing $k$. For $k > 1 \times 10^{-4}$ s$^{-1}$ the concentration of TMOS is almost zero in the oil phase, and the increase of the average $S_w$ with $k$ is due to the fact that an
excess of mixture (2 PV) was injected. The average total amount of silicic acid and the average fraction of silicic acid in the aqueous phase are given in Figure 8.7 as well. Both parameters increase with increasing $k$.

![Graph](image)

**Fig. 8.8:** Calculated final values (at $t = 20$ hours) for the average water saturation $S_w$, amount of silicic acid $w_{wSA} \times S_w$ and fraction of silicic acid $w_{wSA}$. In the simulation the batch size was 2 PV. (left) variation of PV injected. (right) variation of $\varepsilon_0$.

The effect of the injection rate $Q$ on the aforementioned average output parameters is shown in the right-hand graph of Figure 8.7. The rate was varied between 0.02 and 10 ml min$^{-1}$. The final average water saturation decreases with increasing $Q$. With $Q$ in the range of 0.02 to 0.1 ml min$^{-1}$ the amount of SA formed is approximately constant. For values of $Q$ greater than 0.1 ml min$^{-1}$ the amount of SA formed decreases slightly with increasing $Q$, given the amount of mixture injected (2 PV).

In case of an excess amount of mixture injected the amount of silicic acid formed slightly increases with increasing number of PV injected, the degree of which depends on the reaction rate $k$. In this example ($k = 0.323 \times 10^{-3} \text{ s}^{-1}$) the output parameters increase with an increasing number of PV injected for volumes greater than 1 PV (see Figure 8.8). Obviously, in case less than 1 PV of mixture is injected, not all oil in place is displaced by TMOS/oil so that the amount of silicic acid formed is less than in the previous examples. Similarly, the values for $a$, $\varepsilon_0$ and $D$ were varied, each within a representative range. The parameters $a$ and $D$ (not shown here) appeared to have a negligible influence on the average output parameters. However, the parameter $\varepsilon_0$ has significant influence on the mass transfer rate and the average output parameters. It can be observed in Figure 8.8 that the final water saturation and the amount of SA formed decrease with increasing $\varepsilon_0$.

### 8.4.4 Case B. Continuous injection: example

The results of one of the simulations for case B are discussed next. The parameters were chosen as follows. The oil/TMOS mixture is injected continuously with a flow rate $Q = 0.1 \text{ ml min}^{-1}$. The diffusion constant $D$ is $10^{-10} \text{ m}^2 \text{ s}^{-1}$ and the reaction constant $k$ is $0.323 \times 10^{-3} \text{ s}^{-1}$. The interaction parameter $\varepsilon_0$ is equal to $2 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}$ and...
8.4. Results and discussion

8.4.5 Case B. Continuous injection: effect of main parameters

The main parameter considered for Case B is the injection rate $Q$. In the left-hand graph of Figure 8.10 the effect of the injection rate $Q$ on the normalized differential pressure $\Delta P_{\text{norm}}$ is demonstrated. The rate $Q$ was varied between 0.1 and 2 ml min$^{-1}$. All profiles

Fig. 8.9: (left) Example simulation of Case B. Shown are the normalized differential pressure $\Delta P_{\text{norm}}$, the average water saturation $S_w$, the normalized average viscosity of the oil phase $\mu_{\text{o,norm}}$ and the average silicic acid fraction $w_{\text{SA}}$ versus PV injected. $Q$ is 0.1 ml min$^{-1}$ and $k$ is $0.323 \times 10^{-3}$ s$^{-1}$. (right) Saturation profiles at different time intervals.

$a = 4$. The total simulation time is 815 minutes. With respect to the results of Case B we focus on the (normalized) differential pressure over the core, $\Delta P_{\text{norm}}$, versus time, which is shown in Figure 8.9 (left-hand graph). It can be observed that $\Delta P_{\text{norm}}$ decreases to 0.5 as the initial pore volume of mixture has been injected. This is attributed to the relatively fast displacement of the oil originally present in the system with the mixture, which has a lower viscosity. The normalized average viscosity of the oleic phase is plotted as well in Figure 8.9 and shows an initial decrease to about 0.45. Subsequently, the differential pressure increases up to the point at which 10 PV are injected. This is due to the concurrent mass transfer of TMOS from oil to water and the resulting increase of the average water saturation $S_w$, and hence, the decreasing average relative permeability for oil. Some profiles of $S_w$ at different time intervals are shown in the right-hand graph of Figure 8.9. As the average water saturation starts to increase it becomes greater than the irreducible water saturation $S_{wi}$ and the relative permeability for water becomes greater than zero. Some water is therefore produced which counteracts the increase of $S_w$ due to the mass transfer. This causes that $S_w$, and hence $\Delta P_{\text{norm}}$, start to decrease after 10 PV has been injected. However, the drainage is slow and some TMOS is still transferred from the oleic to the aqueous phase. Finally, the average fraction of silicic acid $w_{\text{SA}}$ versus the injected amount of mixture is shown in Figure 8.9. The fraction grows from zero to 0.15 in the initial period (5 PV injected) after which is increases gradually to 0.22 in the remainder of the simulation.
Fig. 8.10: (left) The effect of the injection rate $Q$ on the normalized differential pressure profiles. The reaction rate $k$ is $0.323 \times 10^{-3} \text{ s}^{-1}$. (right) The effect of the aqueous phase viscosity $\mu_w$ (see Legend) on the pressure profiles (with $Q = 0.1 \text{ ml min}^{-1}$).

show an initial decrease of $\Delta P_{\text{norm}}$. The minimum pressure, which is found after about 1 PV has been injected, is the lowest for the highest injection rate and increases with decreasing injection rate. The maximum that follows the minimum is the highest for the lowest injection rate and decreases with increasing injection rate. In addition, the amount of PV injected at which the maximum is found increases with increasing $Q$.

Finally, the effect of gelation on the pressure profiles is considered. Though the gel reaction was not taken into account in the model, we can qualitatively analyse the effect by calculating the pressure profiles using a viscosity $\mu_w$ higher than that of water. In absence of a gel reaction model the viscosity can only be chosen constant. The right-hand graph of Figure 8.10 shows the effect of $\mu_w$ on the pressure profiles. The viscosity $\mu_w$ has little influence on the initial decrease of $\Delta P_{\text{norm}}$ since the water is not mobilized in the initial period. However, after the first 10 PV of solution has been injected the water saturation has increased significantly. Hence, the relative permeability of oil is decreased and the water is slowly drained. Given a flow rate $Q$ the pressure increases with increasing viscosity $\mu_w$.

8.5 Conclusion

The physical-mathematical model can be used to simulate the reactive transport mechanisms of TMOS in linear cores or simple reservoirs. The simulated mass transfer profiles agreed well with the experimental mass transfer profiles measured in the core injection experiments, especially for the unbuffered system and the acid-catalyzed system. The sensitivity analysis of the parameters showed that in case of a low injection rate versus a high reaction rate the mass transfer profiles and the profiles of the reaction products become non-uniform. Secondly, lowering the injection rate or increasing the reaction rate promotes a higher end-point water saturation and larger amount of gel formed (provided an excess of mixture was injected). The latter has important implications for the reduc-
tion of oil phase conductivity. In case the mixture is injected continuously the calculated differential pressure profile appears to be well explained by the average oil viscosity in the initial stages and the changes in the water saturation in the later stages. The pressure profiles are dominated by the ratio of the injection rate and the reaction rate. The effect of gelation, in terms of an increased aqueous phase viscosity, is not important in the initial phase of the injection process.
8. Model of reactive transport of an oil-soluble chemical in porous media
Chapter 9

Concluding remarks and outlook

This final chapter contains the main conclusions based on the work described in this thesis. The reactive transport mechanisms are considered first, followed by the conclusions for permeability modification. Finally, the use of TMOS as an OSC for water shut-off is briefly discussed, and an outlook is given for future research.

9.1 Coupled mass transfer and gel reaction

An overview of the main mechanisms and parameters involved in the reactive transport of TMOS is given in Figure 9.1. Predominantly, the mass transfer of TMOS is driven by the hydrolysis reaction in the aqueous phase, both in bulk systems and in porous materials. The hydrolysis rate (hence the mass transfer rate) increases with temperature and is strongly dependent on pH. At a neutral pH the rate is minimum but increases in the presence of acid- or base-catalysts. The transfer of TMOS tends to completion on a time scale of hours. Formation of gel in the aqueous phase before complete transfer does not yield an impermeable barrier and in such case the TMOS continues to transfer. As the mass transfer is limited by the solubility of TMOS in water and the hydrolysis rate, and not by diffusion, it can be described by a coupled partitioning-reaction model.

The condensation reaction is characterized by the time-dependent transverse relaxation time $T_2$ of the aqueous phase. Due to the cross-linking of the hydrolyzed TMOS molecules the $T_2$ decreases with respect to bulk water and reaches a minimum (or plateau) at the gel point. The gel time decreases with increasing temperature and increasing concentration of TMOS initially present in the oleic phase. The condensation rate is maximum at a pH around 6 and minimum in the acid-catalyzed systems.

When a solution of TMOS in oil is forced into a water-wet sandstone at the irreducible water saturation the solution displaces the non-wetting phase. Concurrently the TMOS transfers to the wetting phase and reacts with water on the pore scale. Since the solution is placed in the porous medium with a finite injection rate, the accumulation of TMOS and, hence, the formation of gel is non-uniform (i.e. macroscopically) in case of a high hydrolysis rate versus a slow injection rate. The pore scale mechanisms of the gel reaction were not revealed by the experiments. However, in some of the alkaline systems multi-component $T_2$ spectra were obtained, which indicate that the formation of gel is non-uniform on the pore scale.
9.2 Permeability modification

The placement of TMOS in a water-wet sandstone at the irreducible water saturation, as described above, leads to an increase of the water saturation and a gel reaction in the water phase. After treatment the overall permeability is reduced due to the diminished pore space available for the flow of both water and oil. The water relative permeability is reduced more than the oil relative permeability. The modification of the relative permeabilities is insensitive to pH and temperature in the system, though the mass transfer rate and reaction rates are dependent on temperature and pH (see previous section).

Gel formed inside sandstone under single phase conditions (see Chapter 7) leads to a drastic reduction of the permeability of the stone with a factor of about $10^4$. The intrinsic permeability of TMOS-based gel is between 1 nm$^2$ (for acid-catalyzed solutions) and 100 nm$^2$ (for base-catalyzed solutions) and depends on the concentration of the TMOS precursor. Again, the permeability reduction of the gel-treated stones is insensitive to pH and is also insensitive to the concentration used. The pore-scale mechanism of the permeability modification by the gel treatment is poorly understood and remains an issue which could be addressed in future studies (e.g. using advanced pore-network models).
9.3 Water shut-off treatments

The advantage of using an OSC, such as TMOS, is that it reacts selectively when placed in a reservoir containing both oil and water. In oil-saturated zones the TMOS will only form gel in the presence of connate water. As discussed before this will lead to a decrease of permeability for both oil and water. However, the permeability reduction for oil will be smaller than the permeability reduction for water.

It is advised to limit, in the application of the OSC, the concentration of TMOS in solution below roughly 20%. This should be done in order to limit the amount of gel formed in the oil-producing zones. After shut-in the production is resumed, the flow of oil will be reduced but not hindered. Ideally, the water in the watered-out zones is blocked towards the production well. In case the water channels through the treated oil-saturated zones it will face a reduced relative permeability due to the formed gel. Reservoir models could be used to predict the flow profiles of both oil and water in the near-wellbore after the gel treatment, in order to optimize the treatment procedure.

The reaction of TMOS with water leads to a relatively quick formation of gel, especially at elevated temperatures and in the presence of base catalysts or some other salts. The conditions found in the field vary, but temperatures above 50 °C and the presence of salts [143, 144] are common in downhole reservoirs. When planning a water shut-off treatment the composition of the brine and the temperature downhole should be taken into account. Simple bulk phase experiments could be performed on site to evaluate the gel time. A controlled placement of TMOS in a well-defined near-wellbore region without premature gelation (also in the assembly) is therefore challenging. A preflush of oil could prove to be useful, first of all in order to cool the wellbore area, and secondly to create a non-wetting pathway in the water-saturated zones.

9.4 Outlook

9.4.1 Extended physical-chemical survey

With respect to the chemical mechanisms of the reactive transport the problem was analyzed using a limited set of parameters, in terms of temperature, pH, concentration of TMOS etc. Since the sol-gel reaction is known to be sensitive not only to pH and temperature but also to concentration and type of catalysts (salts) [24] it is recommended to extend the physical-chemical analysis. Furthermore, it would be interesting to study the effect of oil-composition (and viscosity), wettability and rock type on the reactive transport mechanisms.

As opposed to the indirect determination of the gel time (based on \( T_2 \)) one could employ rheological measurements. A few test experiments were performed using a Couette-type rheometer (Contraves Low Shear 40) to determine the dynamic shear modulus of a gelling TMOS solution (see Figure 9.2). A low-frequency oscillating strain with a small amplitude was imposed on the solution. The absolute shear modulus, which is initially around 0.015 Pa, increases to about 8 Pa at the gel time. The relatively low and fluctuating modulus after the steep increase is probably a result of a poor contact between the gel
9. Concluding remarks and outlook

Fig. 9.2: Absolute shear modulus of a gelling TMOS solution measured in a low-frequency oscillatory mode. The gel time is indicated by the steep increase in the modulus at $t \approx 5$ h.

Fig. 9.3: Schematic view of a Couette-type rheometer. The spindle is lowered in the aqueous phase, so that the measured torque is mainly due to the rheological properties of the aqueous phase.

and the rheometer. Nevertheless, the gel time is clearly indicated by the steep increase of the shear modulus. An interesting approach would be to perform a similar measurement of the shear modulus of the aqueous phase in a two-phase system as illustrated in Figure 9.3. A custom, non-metallic rheometer could be developed that could be used in the NMR set-up. This would allow to directly link the measured (complex) viscosity or shear modulus to the transverse relaxation time $T_2$ in the bulk systems.

9.4.2 Fine-tuning of core injection experiments

The core injection experiments could be improved by employing larger cores (e.g. 15 cm in length and 5 cm in diameter). This way the differential pressure measurements, and hence the permeability measurements, become more accurate and robust. Secondly, the drainage or imbibition processes would be less affected by the non-uniform flow development near the inlet and outlet, compared to the case of using smaller cores. A new NMR insert needs to be built when using cores larger than the cores used in this research.

The current insert (in the 0.95 Tesla set-up) has a satisfactory sensitivity and signal-to-noise ratio, considering the limited time of development. However, the NMR insert (or future inserts) could be optimized to obtain the highest possible signal-to-noise ratio and the shortest acquisition times. Dynamic NMR measurements, e.g. during injection, will be possible in large cores provided the acquisition times can be reduced considerably to less than one minute per slice. Improved signal-to-noise will also improve the quality (resolution) of the $T_2$ spectra (of deuterium), so that one could extract more information on the pore scale gel reaction and distribution. Possible solutions to increase signal-to-noise and sensitivity are the use of higher field strengths and/or the use of improved coil design.
9.4.3 Employing chemical shift

In case the use of $^2$H-NMR is not possible, or at least not in a rapid $^1$H-$^2$H-NMR sequence, the oil phase inside a porous material can be distinguished from the water phase by using normal water and by making use of the chemical shift [70]. Differences in the chemical environment of the hydrogen nuclei result in small differences of the resonance frequency, given an external magnetic field $B_0$. The shift in the resonance frequency is referred to as chemical shift and is commonly expressed in terms of parts per million (ppm). The chemical shift of hydrogen in water is about 4–5 ppm with respect to hydrogen in oil. The detection of chemical shift requires a very homogeneous magnetic field, so that the resonances are not shifted or broadened due to magnetic field gradients. This is accomplished by employing first-order or higher-order shimming coils. Measuring the chemical shift of oil and water in a porous material results in a broadening of the resonances. In many "dirty" materials the internal magnetic gradients are such that the resonances become too broad and cannot be distinguished. The separation of the chemical shift in terms of frequency increases with the main magnetic field. However, the internal gradients of the porous material increase as well, and the optimum in $B_0$ should be considered.

Figure 9.4 shows the chemical shift, measured at 4.7 Tesla, of $n$-hexadecane and water in Bentheim sandstone, which was prepared at the residual oil saturation ($S_w \approx 65\%$). The two peaks of oil and water are well-separated, however, the fine-structure of the \text{-CH} resonances for $n$-hexadecane are obscured. Nevertheless, the separation of the \text{-CH} resonances from the \text{-OH} resonances allows to exploit the chemical shift and allows to separate oil from water in the imaging or relaxation time measurements. The following methods can be used, however, only for set-ups which employ pulsed magnetic gradients instead of static gradients. Chemical specific excitation of the spins (e.g. using the CHESS sequence [36]) enables to image a specific resonance without additional acquisition steps (compared to a conventional sequence). However, a relatively long excitation pulse with

Fig. 9.4: Chemical shift ($^1$H-NMR) of $n$-hexadecane and water in Bentheim sandstone, prepared at the residual oil saturation. The measurement was done at 4.7 Tesla.

Fig. 9.5: Saturation map, obtained from a two-step chemical shift imaging sequence, of a core (saturated at $S_w = S_{wi}$). The core is surrounded by an annular layer of water.
a narrow bandwidth (e.g. a truncated and smoothed sinc pulse) is needed, and the slice selection gradient cannot be used during excitation. Simple non-selective excitation pulses can be used in a chemical shift imaging (CSI) sequence, but multiple acquisition steps are needed. A two-step CSI sequence was introduced by Dixon [145]. In this method two similar acquisition steps are performed. In the second step the rephasing part (either a 180° pulse or a rephasing gradient) is shifted in time with respect to the excitation pulse. This causes a phase shift in the detected signal between the first and the second acquisition. The result of an example CSI measurement is given in Figure 9.5. Improved CSI methods were introduced by Borrello et al. [146] and Chang and Edwards [147]. CSI is also possible with static magnetic gradients in case of a Hahn spin echo-like sequence. Finally, the chemical shift can be resolved for each point in a 1D, 2D or 3D image. This requires an additional phase-encoding loop in the sequence [148].

9.4.4 Pore scale effects

Insight in the pore scale distribution of the gel (as a function of reaction rates etc.) is needed in order to understand the effect of the gel on the fluid conductivity inside the pores. Besides a rigorous analysis of high-quality NMR $T_2$ spectra one could employ micro-CT, though only for small samples having relatively large pores, such as the Bentheim sandstone (see Figure 6.2). On a macro-pore scale the reactive transport and gel formation can be analyzed inside glass bead packs using NMR imaging. Test experiments have revealed interesting behavior of the propagating reaction front in such systems (see also Ref. [43]), but a full analysis remains to be done. Figure 9.6 shows two $T_1$-weighted NMR images of a glass bead pack (with a bead size of about 3 mm) saturated with water in the lower part and with oil/TMOS in the upper part. Like in bulk the TMOS transfers between both phases leading to a change in volume of both phases. Gravity is still important in the macro-porous system, since the oleic phase is always separated from the aqueous phase on the scale of the total system. The overall process of mass transfer is the same as in bulk, but does not occur uniformly across the oil-water contact. Interestingly, the mass transfer appeared to proceed in sudden steps that are fast compared to the overall mass transfer rate. These steps occurred once the oil-water contact was close to the macro-pore, provided that the local concentration of TMOS was still high enough to allow for mass transfer. This is demonstrated by the local signal intensities of the macro-pores as a function of time (see Figure 9.7). Two regions of interest (ROI) were assigned close to the initial oil-water contact at an equal height. The signal intensities within these ROIs increased gradually as the concentration of the TMOS decreased, up to the point where the water quickly invaded the ROIs, which was at completely different times ($t_R = 4$ h and $t_R = 9$ h for ROI 1 and ROI 2, respectively). The images indicate that capillary effects become important even in this macro-porous system, and the irregular sudden invasions resemble so-called Haines jumps [149].

9.4.5 Modeling

Finally, the (numerical) modeling of the reactive transport of TMOS in two-phase systems, both in bulk as in porous systems, could be taken a step further. An interesting approach
Fig. 9.6: $T_1$-weighted NMR images of a glass bead pack saturated with water (lower phase) and oil/TMOS (upper phase). The images were acquired at the beginning of the experiment (left frame), and after 17 hours (right frame), respectively. Region of interests (ROIs) are indicated in the left panel by the white rectangles.

Fig. 9.7: Average NMR signal intensity of the ROIs in the glass bead pack (see Figure 9.6 for details) as a function of time.
is to adopt a non-equilibrium thermodynamical model (Cahn-Hilliard models [150] or diffusive interface models [151]) and to include the description of multi-components and chemical reactions. With a proper free energy expression the effect of solubility of TMOS both in oil and water can be modeled, and thus also the partitioning behavior of TMOS. Such a model could be used both for bulk systems as for pore-scale models.

As noted in Section 9.3 a reservoir model could be used to simulate the gel placement and flow profiles (after treatment) on the the scale of a reservoir. This would answer the question for which situation (i.e. reservoir structure, water breakthrough scenario, etc.) the gel treatment works best, and also how the procedure could be optimized.
Appendix A

Nuclear Magnetic Resonance principles and set-up

A.1 Semi-classical theory of NMR

In analogy to the electron, the spinning motion of the atomic nucleus gives rise to an intrinsic angular momentum denoted by the spin quantum number $I$. For elements having $I > 0$ the spinning motion and the charge distribution result in a nuclear magnetic moment $\mu$, the magnitude of which is given by

$$|\mu| = g\mu_N\sqrt{I(I+1)}, \quad (A.1)$$

where $g$ is the Landé factor ($\approx 5.58$ for the proton) and $\mu_N$ is the nuclear magneton ($\approx 5.05 \times 10^{-27}$ J Tesla$^{-1}$).

From a classical point of view an external magnetic field acts on the nucleus by exerting a torque in order to have it aligned with the direction of the field. In case the nucleus is not already aligned with the field, the torque on the spinning nucleus will result in a precessional motion of the nucleus. The frequency of the precessional motion is proportional to the externally applied field $B_0$, and is called the Larmor frequency $\omega_L$, given by

$$\omega_L = \gamma B_0, \quad (A.2)$$

where $\gamma$ is the gyromagnetic ratio. The ratio is 42.58 MHz Tesla$^{-1}$ for hydrogen and 6.54 MHz Tesla$^{-1}$ for deuterium. Suppose $B_0$ is directed in the $z$-direction, so that $B_0 = B_0 e_z$. When an ensemble of nuclei is magnetized by $B_0$, the nuclei start to precess around an axis parallel to $B_0$. A net magnetization is obtained which is explained by quantum mechanics. The nuclei are forced into a certain energy state. For nuclei with spin quantum number $1/2$, like hydrogen nuclei, there are only two states. The energy splitting, i.e. Zeeman splitting, $\Delta E$ is proportional to $B_0$:

$$\Delta E = \gamma \hbar B_0, \quad (A.3)$$

where $\hbar$ is Planck’s constant. When the precessional axis of the nucleus is parallel to the direction of $B_0$ the nucleus is in the low-energy, that is the preferred state. When the precessional axis is anti-parallel to $B_0$ the nucleus is in the higher energy state (see Figure A.1). Transitions between the two states are induced when the nuclei are subjected to an EM wave with a frequency $\omega$ close or equal to the Larmor frequency $\omega_L$. A net magnetization $M$ is found when the number of nuclei parallel aligned to $B_0$ is larger than anti-parallel, so that

$$M = \sum_i \mu_i = M_0 e_z. \quad (A.4)$$
Fig. A.1: Zeeman splitting of energy of an ensemble of nuclei ($I = 1/2$) in an external magnetic field $B_0$. The partitioning between the energy states is perturbed by an oscillating field with a frequency $\omega = \Delta E/h$.

The magnetization follows from Curie’s law:

$$M_0 = N \frac{\gamma^2 \hbar^2 I(I + 1)}{3k_B T} B_0,$$

(A.5)

where $N$ is the number of nuclei (or spins), $k_B$ is the Boltzmann constant, and $T$ is the temperature. At equilibrium the transverse components $M_x$ and $M_y$ are zero because the nuclei precess out of phase. The basis in NMR lies in the application of an oscillating magnetic field $B_1$ perpendicular to $B_0$. This field is applied using an rf transmission coil. When the field is switched on at the resonance frequency the magnetization, i.e. the balance between the spins in the upper- and lower-energy state is changed. Secondly the spins will start to precess in phase. In the classical view the oscillating field $B_1$ acts on the magnetization vector $\mathbf{M}$ such that it spirals down towards the $x$-$y$ plane with respect to the laboratory frame of reference. The change of the magnetization vector is described by

$$\frac{d\mathbf{M}}{dt} = \gamma (\mathbf{M} \times \mathbf{B}_1).$$

(A.6)

The rotating frame of reference is aligned with the $z$-axis, but by definition rotates with the Larmor frequency with respect to the laboratory frame of reference. In this rotating frame, $(x', y', z')$, the magnetization vector $\mathbf{M}$ rotates due to the torque in a plane perpendicular to the direction of $\mathbf{B}_1$. An rf pulse with duration $\tau$ will rotate the vector over the so-called flip angle $\theta$ (see Figure A.2), which is given by

$$\theta = \gamma B_1 \tau.$$

(A.7)

In the NMR apparatus the magnetization from the nuclei is always measured in the transversal plane. Suppose the magnetization is tipped to the transversal plane by application of a 90° pulse. The magnetization $M_T$, which precesses with the Larmor frequency, is picked up by the rf receiver coil. The received frequencies are around the Larmor frequency of the nuclei. In the remainder we will consider the envelope or amplitude only. The coherence in the precession of the spins is gradually lost (see Figure A.2), because due
Nuclear Magnetic Resonance principles and set-up

![Diagram of magnetic fields and spins](image)

**Fig. A.2:** Tipping of magnetization (in the rotating frame of reference) by application of a $90^\circ$ rf pulse. The obtained transverse magnetization decays due to dephasing of the spins.

To field inhomogeneities and due to spin-spin interaction the spins experience a perturbed local field, resulting in a spread in the Larmor frequency: $\Delta \omega$. For hydrogen nuclei, the spin-spin interaction is in the form of magnetic dipole interaction. The loss in coherence, thus the decrease in net magnetization is described by an exponential decay:

$$M_T(t) = M_0 \exp \left( -\frac{t}{T_2^*} \right),$$  \hspace{1cm} (A.8)

where $T_2^*$ is the relaxation time due to spin-spin interaction and field inhomogeneities.

The decay described by Eq. A.8 is referred to as the free induction decay (FID). In an NMR experiment the FID signal can be partly restored. The effect of static inhomogeneities in $B_0$ is reversed by the so called spin echo \[152\] detection which forms the basis of many NMR measurement methods \[50\]. A spin echo is formed by applying a $180^\circ$ rf pulse after the first $90^\circ$ pulse. Suppose this pulse is timed at $t = T_E/2$, then the echo is found exactly at $t = T_E$, which is termed the echo time (see Figure A.3). Although part of the FID signal decay is restored, some irreversible loss of coherence is still present due to spin-spin interactions. The magnitude of the spin echo $S$ is described by an exponential decaying function, i.e.

$$S(t = T_E) = S_0 \exp \left( -\frac{T_E}{T_2} \right),$$  \hspace{1cm} (A.9)

**Fig. A.3:** Schematic of spin echo sequence. The $90^\circ$ pulse is followed by the free induction decay (FID). By applying a $180^\circ$ pulse at $t = \frac{1}{2}T_E$ an echo is formed at $t = T_E$, where $T_E$ is the echo time. The magnitude of the echo is described by an exponential relaxation function with relaxation time $T_2$. 
where $S_0$ is a constant proportional to $M_0$, and $T_2$ is the transverse or spin-spin relaxation time. As the magnetization is tipped to the transversal plane by the 90° the longitudinal magnetization $M_z$ is zero but restores to the equilibrium magnitude $M_0$ in the course of time due to energy transfer between the spins and the thermal reservoir (lattice). The magnetization restores with an exponential function given by

$$M_z(t) = M_0 \left[ 1 - \exp \left( -\frac{t}{T_1} \right) \right], \quad (A.10)$$

where $T_1$ is the longitudinal or spin-lattice relaxation time. In case of hydrogen the relaxation processes are driven by dipole-dipole interactions among the protons [51].

Fig. A.4: The two NMR set-ups used for the experiments. (left) 4.7 Tesla super-conducting magnet (Oxford, Oxon, UK) with a 3D-imaging, pulsed-gradient insert (Doty, Columbia, SC, USA). (right) 0.95 Tesla iron-cored electromagnet with a home-built insert equipped with a 1D static gradient. The insert is designed to measure both hydrogen and deuterium.

A.2 NMR set-up

Two NMR scanners were employed for the experiments (see Figure A.4). The first system, consisting of a 4.7 Tesla super-conducting magnet and a 3D-imaging insert with pulsed gradients, was used for the first set of bulk experiments and the IFT analysis (see Chapters 2 and 3). The second system, consisting of a 0.95 Tesla iron-cored electromagnet and home-built insert, was used for the second set of bulk experiments (see Chapter 4) and for the core injection experiments (see Chapter 6).

The 4.7 Tesla scanner has a vertical insert with an inner diameter of 40 mm and is equipped with a set of three pulsed magnetic gradients for imaging purposes. The rf circuit contains a Litz volume coil [153] and three adjustable capacitors for tuning and impedance matching. A duplexer is used to separate the transmitted rf power from the received rf signal. A schematic of the set-up is shown in Figure A.5. The circuit is designed for hydrogen and is tuned at 200 MHz.
Fig. A.5: Schematic of the rf front-end and data acquisition system (DAS) of the 4.7 Tesla NMR scanner.

Fig. A.6: Schematic of the rf front-end and data acquisition system (DAS) of the 0.95 Tesla NMR scanner.
The 0.95 Tesla scanner has a vertical insert with an inner diameter of 31 mm. The insert was designed to measure both hydrogen (at 40.5 MHz) and deuterium (at 6.23 MHz). Two different rf circuits are used which share a single solenoid coil (see Figure A.6). The coil is wound around a Faraday shield which reduces the effect of variations in the dielectric permittivity of the sample on the tuning [154]. A switch is placed between the coil and the two rf circuits which allows for fast toggling between the measurement of hydrogen or deuterium. Each circuit has its own duplexer tuned at the proper frequency. The frequency of the transmitted rf power is set by the transmitter. The rf power is fed to one of the duplexers through a relay. Another relay is used to connect the proper duplexer to the amplifier for the incoming rf signal which is further processed in the data acquisition system (DAS). The (mechanical) switch and both relays are controlled by the DAS. A set of Anderson coils is used to produce a 1D static gradient in the vertical direction. Both scanners are operated using software developed in the laboratory [155].
Appendix B

Derivation of partitioning equation

In this appendix the Gibbs free energies of mixing for both phases are defined from which the expressions for the chemical potentials of TMOS in either phase are derived. The differences in molecular sizes are neglected. The oil consists of a single representative hydrocarbon. The free energy of mixing of the oleic phase $G_o$ is given by

$$\beta G_o = n_o \ln \frac{n_o}{n_o + m_o} + m_o \ln \frac{m_o}{n_o + m_o}, \quad (B.1)$$

where $\beta = (R_g T)^{-1}$, $n_o$ is the number of TMOS molecules in the oleic phase and $m_o$ is the number of hydrocarbon molecules. The chemical potential of TMOS in oil $\mu_o$ follows from a derivation of the free energy, i.e.

$$\beta \mu_o = \left( \frac{\partial \beta G_o}{\partial n_o} \right)_{T,p,m_o} = \ln \frac{n_o}{n_o + m_o}. \quad (B.2)$$

In the aqueous phase there is an extra contribution to the free energy $G^*$ due to the interaction of TMOS with water, which favors or hinders the mixing. The free energy of mixing of the aqueous phase $G_w$ is given by

$$\beta G_w = n_w \ln \frac{n_w}{n_w + m_w} + m_w \ln \frac{m_w}{n_w + m_w} + \beta G^*, \quad (B.3)$$

where $n_w$ is the number of TMOS molecules in the aqueous phase and $m_w$ is the combined number of water, methanol and silicic acid molecules. Hence, the chemical potential of TMOS in water $\mu_w$ becomes

$$\beta \mu_w = \left( \frac{\partial \beta G_w}{\partial n_w} \right)_{T,p,m_w} = \ln \frac{n_w}{n_w + m_w} + \beta \frac{\partial G^*}{\partial m_w}. \quad (B.4)$$

The interaction term is defined as

$$G^* = n_w \varepsilon(n_m), \quad (B.5)$$

where $\varepsilon$ is an interaction parameter that depends on the methanol concentration $n_m$. Equating the chemical potentials $\mu_o$ and $\mu_w$ leads to the partitioning expression

$$\frac{n_w}{n_w + m_w} = \frac{n_o}{n_o + m_o} \exp \left( -\frac{\varepsilon(n_m)}{R_g T} \right). \quad (B.6)$$
Appendix C

Effect of slip on bending experiment

In this appendix we analyze the effect of slip on the measured load $W$ in a three-point beam bending experiment. The effect of slip is modeled in the form of a time-dependent deflection term, i.e. $\Delta = \Delta(t)$. The strain $\varepsilon_z$ is directly proportional to the deflection, therefore $\varepsilon_z = \varepsilon_z(t)$. In the following we consider a rectangular elastic plate (as was described in the Section 7.2). The plate is saturated with a Newtonian fluid. The constitutive equations are \[131\]

\[\varepsilon_x = \frac{1}{E_p} [\sigma_x - \nu_p(\sigma_y + \sigma_z)] - \frac{\hat{b}}{3K_p} P,\]

\[\varepsilon_y = \frac{1}{E_p} [\sigma_y - \nu_p(\sigma_x + \sigma_z)] - \frac{\hat{b}}{3K_p} P,\]

\[\varepsilon_z = \frac{1}{E_p} [\sigma_z - \nu_p(\sigma_x + \sigma_y)] - \frac{\hat{b}}{3K_p} P,\]

where $\sigma$ is the pore stress, $P$ is the stress in the fluid, which is equal to the pressure but opposite in sign, and $\hat{b}$ is the Biot coefficient defined by

\[\hat{b} = 1 - \frac{K_p}{K_S}.\]

After the beam is bent the pressure in the pore fluid is dissipated due to flow of the fluid within the pores. The continuity equation is given by \[131\]

\[\frac{\partial P}{\partial \theta} = \frac{\partial^2 P}{\partial v^2} + \kappa \frac{\partial^2 P}{\partial w^2} + \frac{E_p \hat{b} \partial \varepsilon_z}{3 \mu},\]

where $\mu$ reads

\[\mu = \frac{(1 - \rho)K_p}{K_L} + \left(\frac{\rho - K_p/K_S}{K_p}K_p + \frac{2(1 + \nu_p)}{3} \left(1 - \frac{K_p}{K_S}\right)^2.\]

The solution of Eq. C.5 with the usual boundary conditions ($P = 0$ at the boundary) is given by \[131\]

\[P(v, w, \theta) = \frac{8E_p \hat{b} \varepsilon_z}{\mu L^3} \int_0^\theta \Omega_A(\theta - \theta') \Omega_B[\kappa(\theta - \theta')] \frac{d\Delta}{d\theta'} d\theta',\]

\[\text{C.7}\]
where
\[
\Omega_A(\theta) = -2 \sum_{m=1}^{\infty} \frac{(-1)^m}{a_m} \sin(a_m \theta) \exp(-a_m^2 \theta),
\] (C.8)
\[
\Omega_B(\theta) = 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{b_n} \cos(b_n \theta) \exp(-\kappa b_n^2 \theta),
\] (C.9)
and \(a_m = m\pi\), \(b_n = (2n-1)\pi/2\). The load required to sustain the deflection follows from integration of the total stress:
\[
W(t) = -\frac{2a^2 b}{z} \int_{-1}^{1} \int_{-1}^{1} E_p \left( \frac{\dot{b}}{3K_p} P + \varepsilon_z \right) v dv dw,
\] (C.10)
where the strain is given by
\[
\varepsilon_z = -\frac{24a z v}{L^3} \Delta.
\] (C.11)
Working out the integrals in Equation C.10 yields
\[
W(\theta) = c_1 \Delta(\theta) + c_2 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{a_m^2 b_n^2} \exp[-\theta(a_m^2 + \kappa b_n^2)] \int_0^{\theta} \exp[\theta'(a_m^2 + \kappa b_n^2)] \frac{d\Delta}{d\theta'} d\theta',
\] (C.12)
where
\[
c_1 = \frac{192a^3 b E_p}{3L^3},
\] (C.13)
\[
c_2 = \frac{256a^3 b E_p^2 \hat{b}^2}{3\mu L^3 K_p}.
\] (C.14)
An analytical solution is obtained when the deflection follows an exponential decay, for example
\[
\Delta = \Delta_0 H(\theta) \left[ (1 - h) + h \exp \left( -\frac{\theta \tau_R}{\tau_S} \right) \right],
\] (C.15)
where \(H\) is the Heaviside step function, \(h\) reflects the amount of slip (0 \(\leq\) \(h\) \(\leq\) 1, and \(h = 0\) implies no slip) and \(\tau_S\) is a decay rate. Substituting Eq. C.15 in Eq. C.12 yields
\[
W(\theta) = c_1 \Delta(\theta) + c_2 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \Delta_0 \frac{\Delta_0}{a_m^2 b_n^2} \left\{ \exp(-\theta \Gamma_{nm}) + \frac{h \tau_R}{\tau_R - \tau_S \Gamma_{nm}} \right\} \left\{ \exp \left[ -\theta \left( \frac{\tau_R}{\tau_S} - \Gamma_{nm} \right) \right] - \exp[-\theta \Gamma_{nm}] \right\},
\] (C.16)
where \(\Gamma_{nm} = a_m^2 + \kappa b_n^2\).

It can be shown that Eq. C.16 reduces to the usual hydrodynamic relaxation expression when \(h = 0\). In case of slip, i.e. \(h > 0\), the decreasing deflection results in an inflection in the load curve similar to that of the hydrodynamic contribution. Some model calculations were performed for an elastic porous plate filled with glycerol and having a permeability of
Fig. C.1: Calculated load curves for an elastic porous plate, with a permeability of 10 nm², an elastic modulus of 10 GPa and filled with glycerol. The hydrodynamic relaxation time $\tau_R$ is equal to 159 s and $A = 0.042$. The deflection decays exponentially with a relaxation time $\tau_S$ equal to $\lambda \tau_R$ and $h = A$. The ratio $\lambda$ was varied and is indicated in the legend.

10 nm² and an elastic modulus of 10 GPa. The resulting curves are shown in Figure C.1. The amount of hydrodynamic relaxation $A$ is equal to 0.042 and $h = A$. We note that the relaxation data for the gel-filled stones imply that $h$ is larger (up to 0.3) in some cases. The relaxation time $\tau_R$ equals 159 s. When $\tau_S \gg \tau_R$ the second inflection due to slipping is well separated from the primary inflection. In case $\tau_S \ll \tau_R$ the primary inflection in the load curve is brought about by the effect of slip and the second inflection is due to hydrodynamic relaxation. When $\tau_S \approx 0.1 \times \tau_R$ the effects cannot be distinguished, nevertheless the time at which the inflection is found is still close to $0.2 \times \tau_R$. 
Appendix D

Phase density approximation

The phase densities $\rho_o$ and $\rho_w$ are functions of pressure and composition. The derivative of the density of phase $\alpha$ with respect to time is given by

$$\frac{\partial \rho_\alpha}{\partial t} = \sum_X \frac{\partial \rho_\alpha}{\partial w_\alpha^X} \frac{\partial w_\alpha^X}{\partial t} + \frac{\partial \rho_\alpha}{\partial P_\alpha} \frac{\partial P_\alpha}{\partial t}. \quad (D.1)$$

An average compressibility, $c_\alpha$, of phase $\alpha$ is defined such that

$$c_\alpha = \frac{1}{\rho_\alpha} \frac{\partial \rho_\alpha}{\partial P_\alpha}. \quad (D.2)$$

Assuming ideal mixing, at constant pressure the density of phase $\alpha$ is given by

$$\frac{1}{\rho_\alpha} = \sum_X w_\alpha^X \varrho_X, \quad (D.3)$$

where $\varrho_X$ is the density of component $X$ in a pure liquid. The partial derivatives of $\rho_\alpha$ with respect to the mass fractions $w_\alpha^X$ become complicated, especially when the number of components is greater than two. However, in terms of volume fractions, $\phi_\alpha^X$, the phase density reads

$$\rho_\alpha = \sum_X \phi_\alpha^X \varrho_X. \quad (D.4)$$

For a two-component mixture the volume fraction $\phi$ is related to the mass fraction $w$ by

$$\phi = \frac{w \varrho_2}{w \varrho_2 + (1 - w) \varrho_1}. \quad (D.5)$$

When $\varrho_1 \approx \varrho_2$ the volume fraction $\phi$ is approximately equal to $w$. Similarly, in a multi-component mixture the volume fractions are approximately equal to the mass fractions when the densities of the pure components are approximately equal to each other. The time derivative of the phase density can be simplified by assuming that

$$\rho_\alpha \approx \sum_X w_\alpha^X \varrho_X, \quad (D.6)$$

so that Eq. D.1 becomes

$$\frac{\partial \rho_\alpha}{\partial t} = \sum_X \varrho_X \frac{\partial w_\alpha^X}{\partial t} + c_\alpha \rho_\alpha \frac{\partial P_\alpha}{\partial t}. \quad (D.7)$$
Appendix E

Numerical discretization of model

A one-dimensional grid is defined with $N$ grid blocks of size $\Delta z$. The mobility parameter and phase density are weighed upstream. The time step of integration is given by $\Delta t$. The oil pressure is solved for using a discretized scheme in the following form (see Valiollahi 2005 [140] for details):

$$a P_{o,i+1}^{n+1} + b P_{o,i}^{n+1} + c P_{o,i-1}^{n+1} = d,$$  

(E.1)

where $P_{o,i}^{n}$ represents the oil pressure in grid block $i$ at time step $n$. The coefficients in Eq. E.1 for the regular grid blocks ($1 < i < N$) are given by (the sub- and superscript of $U_w$ are omitted)

$$a = -\left(\lambda_{o,i}^{n} + \lambda_{w,i}^{n}\right),$$

$$b = \left(\lambda_{o,i}^{n} + \frac{\rho_{o,i}^{n-1}}{\rho_{o,i}^{n}} \lambda_{o,i-1}^{n} + \frac{\rho_{w,i-1}^{n}}{\rho_{w,i}^{n}} \lambda_{w,i-1}^{n}\right) + \frac{\varphi \Delta z^2}{\Delta t} (S_o c_o + S_w c_w)^n_i,$$

$$c = -\left(\frac{\rho_{o,i-1}^{n}}{\rho_{o,i}^{n}} \lambda_{o,i-1}^{n} + \frac{\rho_{w,i-1}^{n}}{\rho_{w,i}^{n}} \lambda_{w,i-1}^{n}\right),$$

$$d = \frac{\varphi \Delta z^2}{\Delta t} \left[ (S_o c_o + S_w c_w)^n_i P_{o,i}^{n} - \left(\frac{s_o}{\rho_o}\right)_i^n \sum_{l} g_{1,l}^{n} \left(w_{o,i}^{l,n} - w_{o,i}^{l,n-1}\right) \right. $$

$$- \left. \left(\frac{s_w}{\rho_w}\right)_i^n \sum_{l} g_{1,l}^{n} \left(w_{w,i}^{l,n} - w_{w,i}^{l,n-1}\right) \right]$$

$$- \lambda_{w,i}^{n} \left(P_{c,i+1}^{n} - P_{c,i}^{n}\right) + \frac{\rho_{w,i-1}^{n}}{\rho_{w,i}^{n}} \lambda_{w,i-1}^{n} \left(P_{c,i}^{n} - P_{c,i-1}^{n}\right) + \Delta z^2 \left(\frac{1}{\rho_{w,i}^{n}} - \frac{1}{\rho_{w,i}^{n-1}}\right) U_i^n.$$  

(E.2)

Hence, the pressure is updated by solving the following matrix equation

$$MP^{n+1} = d,$$  

(E.3)

where $M$ is a tri-diagonal matrix comprising the defined terms $a$, $b$ and $c$.

The inlet boundary condition is taken into account through the equation

$$a_1 P_{o,2}^{n+1} + (b_1 + c_1) P_{o,1}^{n+1} = d_1 - c_1 \frac{q_o \rho_{o,sc} \Delta z}{A P_o \lambda_o},$$  

(E.4)

where $\rho_{o,sc}$ is the oil density at standard conditions, $q_o$ is equal to $Q$ in the injection step.
and equal to zero in the shut-in step. The coefficients \( a_1, b_1, c_1 \) and \( d_1 \) are given by

\[
a_1 = -\left(\lambda^n_{o,1} + \lambda^n_{w,1}\right),
\]

\[
b_1 = 2(\lambda^n_{o,1} + \lambda^n_{w,1}) + \frac{2\Delta z^2}{\Delta t} (S_o c_o + S_w c_w)_1^n,
\]

\[
c_1 = -\left(\lambda^n_{o,1} + \lambda^n_{w,1}\right),
\]

\[
d_1 = \frac{\Delta z^2}{\Delta t} \left[(S_o c_o + S_w c_w)^n_1 P_{o,1}^n - \left(\frac{S_w}{\rho_o}\right)^n_1 \sum_I \mathcal{I}_{I,n} \left(w_{o,1}^n - \omega_{o,1}^{n-1}\right) - \left(\frac{S_w}{\rho_o}\right)^n_1 \sum_I \mathcal{I}_{I,n} \left(w_{w,1}^n - w_{w,1}^{n-1}\right)\right]
\]

\[
-\lambda^n_{o,1} (P_{c,2}^n - P_{c,1}^n) - \frac{\Delta z}{\rho_w^2} \left(\frac{q_o \rho_w \lambda_o \rho_o \lambda_o}{\rho_o^2} - \frac{1}{\rho_o^2} \lambda_o \right) \Delta z^2 \left(P_{c,1}^n - 1\right) + \Delta z^2 \left(\frac{1}{\rho_{w,1}^2} - \frac{1}{\rho_{o,1}^2}\right) U_1^n.
\]  

(E.5)

The outlet boundary condition is taken into account through the equation

\[
(b_N - a_N) P_{o,N}^{n+1} + c_N P_{o,N-1}^{n+1} = d_N - 2a_N P_{out},
\]  

(E.6)

in which the coefficients are given by

\[
a_N = -\left(\lambda^n_{o,N} + \lambda^n_{w,N}\right),
\]

\[
b_N = \left(\lambda^n_{o,N} + \lambda^n_{w,N} + \frac{\rho_o^2}{\rho_o^2} \lambda^n_{o,N-1} + \frac{\rho_o^2}{\rho_o^2} \lambda^n_{w,N-1}\right) + \frac{\Delta z^2}{\Delta t} (S_o c_o + S_w c_w)_N^n,
\]

\[
c_N = -\left(\frac{\rho_o^2}{\rho_o^2} \lambda^n_{o,N-1} + \frac{\rho_o^2}{\rho_o^2} \lambda^n_{w,N-1}\right),
\]

\[
d_N = \frac{\Delta z^2}{\Delta t} \left[(S_o c_o + S_w c_w)_N^n P_{o,N}^n \right.
\]

\[
-\left(\frac{S_w}{\rho_o}\right)^n_N \sum_I \mathcal{I}_{I,n} \left(w_{o,1}^n - \omega_{o,1}^{n-1}\right) \left(\frac{S_w}{\rho_o}\right)^n_N \sum_I \mathcal{I}_{I,n} \left(w_{w,1}^n - w_{w,1}^{n-1}\right)\]

\[
+\lambda^n_{w,N} P_{c,N}^n \left(\frac{P_{c,N}^n}{\rho_o^2} - \frac{P_{c,N-1}^n}{\rho_o^2}\right) + \Delta z^2 \left(\frac{1}{\rho_{w,N}^2} - \frac{1}{\rho_{o,N}^2}\right) U_N^n.
\]  

(E.7)

**Update of oil saturation and composition**

The oil saturation is updated explicitly using the following discretized equation

\[
S_{o,i}^{n+1} = \frac{\rho_o}{\rho_{o,i}} S_{o,i}^n + \frac{\Delta t}{\varphi \rho_{o,i}} \left[\left(\rho_o \lambda_o\right)^n_{i} \frac{P_{o,i}^{n+1} - P_{o,i}^{n+1}}{\Delta z^2} - \left(\rho_o \lambda_o\right)^n_{i-1} \frac{P_{o,i-1}^{n+1} - P_{o,i-1}^{n+1}}{\Delta z^2} - U_i^n\right].
\]  

(E.8)

With respect to the inlet boundary condition we have

\[
S_{o,1}^{n+1} = \frac{\rho_o}{\rho_{o,1}} S_{o,1}^n + \frac{\Delta t}{\varphi \rho_{o,1}} \left[\left(\rho_o \lambda_o\right)^n_{1} \frac{P_{o,2}^{n+1} - P_{o,1}^{n+1}}{\Delta z^2} + \frac{q_o \rho_o \lambda_o}{\rho_o^2} - U_1^n\right],
\]  

(E.9)
and for the outlet:
\[
S^{n+1}_{o,N} = \frac{\rho^o_{o,N}}{\rho^o_{w,N}} S^n_{o,N} + \Delta t \frac{\varphi}{\varphi_{o,Nw}} \left[ 2 \left( \rho^o_{o,N} \frac{n}{\Delta z^2} (P_{out} - P^{n+1}_{o,N}) - \left( \rho^o_{o,N} \frac{n}{\Delta z^2} P^{n+1}_{o,N} - P^{n+1}_{o,N-1} \right) U_n \right) \right].
\] (E.10)

In the following definition \(u^{n+1}_{\alpha,i}\) is the Darcy velocity of phase \(\alpha\) at the outlet of grid block \(i\):
\[
u^{n+1}_{\alpha,i} = - \frac{1}{\Delta z} \lambda^{n+1}_{\alpha,i} \left( P^{n+1}_{\alpha,i+1} - P^{n+1}_{\alpha,i} \right),
\] (E.11)
and for the boundary points we find that
\[
u^{n+1}_{\alpha,0} = u^{n+1}_{\alpha,inj} = \frac{q_0 \rho_{\alpha,sc}}{A \rho^o_{n+1}}; \quad \nu^{n+1}_{\alpha,N} = - \frac{2}{\Delta z} \lambda_{\alpha,N} \left( P_{out} - P^{n+1}_{\alpha,N} \right).
\] (E.12)

The mass fraction \(w^O_o\) is updated by a discretized form of the mass balance equation for oil in the oleic phase, yielding
\[
\left[ \rho^{n+1}_{o,i} S^n_{o,i} + \Delta t \frac{\varphi}{\varphi_{o,i}} \rho^{n+1}_{o,i} u^{n+1}_{o,i} \right] w^{O,n+1}_{o,i} - \left[ \Delta t \frac{\varphi}{\varphi_{o,i}} \rho^{n+1}_{o,i-1} u^{n+1}_{o,i-1} \right] w^{O,n+1}_{o,i-1} = \rho^{n}_{o,i} S^n_{o,i} w^{O,n}_{o,i},
\] (E.13)
which is used for the outlet as well as for the inner grid cells. For the inlet we have:
\[
\left[ \rho^{n+1}_{o,i} S^n_{o,i} + \Delta t \frac{\varphi}{\varphi_{o,i}} \rho^{n+1}_{o,i} u^{n+1}_{o,i} \right] w^{O,n+1}_{o,i} = \rho^{n}_{o,i} S^n_{o,i} w^{O,n}_{o,i} + \Delta t \frac{\varphi}{\varphi_{o,inj}} \rho^{n+1}_{o,inj} u^{n+1}_{o,inj} w^o_i.
\] (E.14)

The fraction of TMOS at time step \(n\) follows from the closure condition: \(w^T_o = 1 - w^O_o\).

**Update of water composition**

The compositions in the aqueous phase are updated implicitly using the following discretized equations (for water, methanol and silicic acid, respectively):
\[
\left( \frac{\varphi}{\Delta t} \rho_w S_w + \frac{1}{\Delta z} u_w \rho_w \right)^{n+1}_{i} w^{W,n+1}_{w,i} = \frac{1}{\Delta z} (u_w \rho_w)^{n+1}_{i-1} w^{W,n+1}_{w,i-1} - \frac{\varphi}{\Delta t} \left( w^{W,n+1}_{w,i} + 4 \varphi M^W S^n_{w,i} R^n_i \right),
\] (E.15)
\[
\left( \frac{\varphi}{\Delta t} \rho_w S_w + \frac{1}{\Delta z} u_w \rho_w \right)^{n+1}_{i} w^{M,n+1}_{w,i} = \frac{1}{\Delta z} (u_w \rho_w)^{n+1}_{i-1} w^{M,n+1}_{w,i-1} - \frac{\varphi}{\Delta t} \left( w^{M,n+1}_{w,i} + 4 \varphi M^W S^n_{w,i} R^n_i \right),
\] (E.16)
and
\[
\left( \frac{\varphi}{\Delta t} \rho_w S_w + \frac{1}{\Delta z} u_w \rho_w \right)^{n+1}_{i} w^{SA,n+1}_{w,i} = \frac{1}{\Delta z} (u_w \rho_w)^{n+1}_{i-1} w^{SA,n+1}_{w,i-1} - \frac{\varphi}{\Delta t} \left( w^{SA,n+1}_{w,i} + \varphi M^W S^n_{w,i} R^n_i \right),
\] (E.17)
As the saturations, densities and fractions are updated the reaction rate $R$ can be calculated using the equation

$$R_{i}^{n+1} = k_h \left[ (\rho_w)^{\beta+\gamma} (w_T^T)^{\beta} (w_w^W)^{\gamma} \right]_{i}^{n+1}.$$  \hfill (E.18)

The mass transfer term $U$ follows from the evaluation of the partitioning function (Eq. 8.15) and the total TMOS density (Eq. 8.16). In discretized form we have

$$\tilde{\rho}_{total,i}^{n+1} = \tilde{\rho}_{o,i}^{n+1} + \tilde{\rho}_{w, i}^{n+1},$$  \hfill (E.19)

$$\tilde{\rho}_{eq,i}^{n+1} = \tilde{\rho}_{total,i}^{n+1} \frac{E}{E+1},$$  \hfill (E.20)

where $E$ is given by

$$E = \exp \left[ \frac{\varepsilon_0 \left( 1 - aw_{w,1}^{M,n+1} \right)}{R_g T} \right].$$  \hfill (E.21)

Subsequently, the mass transfer term reads

$$U_{i}^{n+1} = \frac{4D \phi}{r_w^2 \left[ 1 + \left( S_{\rho,i}^{-1/2} \right)_{i}^{n+1} \right]} \left( \tilde{\rho}_{o,i}^{n+1} - \tilde{\rho}_{eq,i}^{n+1} \right).$$  \hfill (E.22)
Bibliography


Summary

The subject of the thesis is two-phase reactive transport of an Oil-Soluble Chemical (OSC). An OSC is a chemical that is soluble and chemically stable in oil, however it reacts with water to form a gel. A novel concept is the use of OSCs in the oil industry for water control, in order to reduce water production in oil and gas production wells.

The aim of the research was to investigate, on a fundamental level, the reactive transport of an OSC in two-phase systems, in bulk and within porous materials. The chemical tetra-methyl-ortho-silicate (TMOS) was chosen as a model OSC. The choice is inspired by the potential use of TMOS for water shut-off. When a solution of TMOS in oil comes in contact with water the chemical transfers to the water phase where it undergoes a heterogeneous sol-gel reaction. The main experimental tool used to characterize the reactive transport, both in bulk as in porous materials, was Nuclear Magnetic Resonance (NMR).

In Chapter 2 the NMR methods to monitor the reactive transport in bulk systems are introduced and described in detail. TMOS was dissolved in n-hexadecane and placed in (small) vials together with demineralized water. Two-dimensional images of a cross section of the samples were acquired, which revealed qualitatively the mass transfer behavior between both phases. The concentration of TMOS in oil was determined by measuring the longitudinal relaxation time \( T_1 \) of hydrogen in the oleic phase, using calibrations of \( T_1 \) for TMOS in n-hexadecane. Further, the transverse relaxation time \( T_2 \) of hydrogen in the aqueous phase was measured to monitor the progress of gelation. During the gel reaction \( T_2 \) decreases in the course of time and reaches a minimum (plateau) at the gel point. The reduction of \( T_2 \) is caused by the interaction of the water molecules with the silica aggregates and the formation of methanol in the gel reaction.

An image analysis method to determine the interfacial tension (IFT) between both phases in the bulk systems using the NMR images is presented in Chapter 3. The method is based on interface tracking. A second-order boundary value problem, which describes the interfacial energy in terms of the IFT and the effect of gravity, is solved and optimized for each image, yielding the IFT as a function of time. At an initial concentration of 40 vol\% of TMOS in oil the IFT is initially about 10 mN m\(^{-1}\), but it increases gradually to about 20 mN m\(^{-1}\) as the TMOS transfers from oil to water. Also in Chapter 3, a conceptual model is introduced to describe the mass transfer and hydrolysis of TMOS based on a partitioning-reaction model.

In Chapter 4 the use of a bi-nuclear NMR method is introduced. Again bulk systems were considered. In this case the water used was D\(_2\)O. \( T_1 \) of hydrogen in the oleic phase was measured to determine the concentration of TMOS in oil, and \( T_2 \) of deuterium in the aqueous phase was used to characterize the progress of gelation. The experiments showed that the pH of the aqueous phase is the main parameter that influences the mass transfer.
and gelation rates. The mass transfer is predominantly driven by the hydrolysis reaction. At a neutral pH the mass transfer rate is low, but it increases in the presence of acid and base catalysts. The condensation reaction is slow at a low pH but fast at a neutral or high pH.

A phenomenological model to describe the cross-linking (condensation) reaction of hydrolyzed TMOS in the two-phase systems is given in Chapter 5. The number of hydrolyzed TMOS molecules in the water phase is time-dependent and follows from mass transfer profiles which are based on the experimental results. The cross-linking reaction is described using a population balance model. A set of differential equations is obtained, which is solved numerically. The weight-average molecular weight $\bar{M}_w$ of the population diverges at a critical time $t_c$, which decreases with increasing hydrolysis rate, increasing condensation rate or increasing initial concentration of TMOS. Additionally, the profiles of $\bar{M}_w$ versus time were employed to predict qualitatively the $T_2$ profiles from the experiments.

Chapter 6 discusses the results of a series of core injection experiments. TMOS dissolved in oil was injected in Bentheim sandstone at the irreducible water saturation. Bi-nuclear NMR measurements were performed to monitor the reactive transport in situ. Like in bulk systems the mass transfer in sandstone is driven by the hydrolysis reaction. Both the mass transfer rate and gelation rate are dependent on pH and temperature, and similar trends as in the bulk systems were observed. The placement and reaction of TMOS in sandstone at the irreducible water saturation leads to a reduction of the water permeability greater than the reduction of the oil permeability.

A beam bending method was employed to measure the effect of gel, which was formed in situ under single phase conditions, on the permeability of sandstone. The results are discussed in Chapter 7. Beam bending measurements on TMOS-based gel rods revealed that the permeability of acid-catalyzed gels is on the order of 1 nm$^2$, when the silica fraction is approximately 10%. Base-catalyzed gels have a permeability on the order of 10 to 100 nm$^2$ for similar concentrations. When a gelling solution is imbibed in sandstone, the formed gel leads to a reduction of the permeability of the stone by a factor of about $10^4$. The reduction is insensitive to the pH and concentration used.

In Chapter 8 a physical-mathematical model is presented which describes the reactive transport of TMOS (or other OSCs) in porous materials. The model can be used to simulate numerically the placement of TMOS in linear cores or in simple reservoirs. A number of calculations was performed to simulate the core experiments described in Chapter 6. The simulated mass transfer profiles agreed well with the experimental mass transfer profiles, especially for the unbuffered system and the acid-catalyzed system. In a second series of simulations the mixture was injected continuously. The differential pressure profiles are well explained by the average oil viscosity in the initial stages and the changes in the water saturation in the later stages. The pressure profiles are dominated by the injection rate versus the reaction rate. The effect of gelation, in terms of an increased aqueous phase viscosity, is not important in the initial phase of the injection process.
Samenvatting

Het onderwerp van het proefschrift is reactief transport van een Oil-Soluble Chemical (OSC) in tweefasesystemen. Een OSC is een stof die oplosbaar en chemisch inert is in olie, maar die reageert met water om een gel te vormen. Een nieuw concept in de olieindustrie is het gebruik van OSC’s voor waterregulering, om zodoende de waterproductie in olievelden en gasbronnen te reduceren.

Het doel van het onderzoek was het bestuderen, op een fundamenteel niveau, van het reactief transport van een OSC in tweefasesystemen, zowel in bulk als in poreuze materialen. De stof tetra-methyl-ortho-silicate (TMOS) was gekozen als een model-OSC. De keuze was geïnspireerd door het potentieel gebruik van TMOS voor waterafsluiting. Wanneer een oplossing van TMOS in olie in contact komt met water dan gaat de stof over in de waterfase, waarin het een heterogene sol-gel-reactie aangaat met water. De belangrijkste experimentele methode die gebruikt werd in dit onderzoek was Nuclear Magnetic Resonance (NMR), ook wel magnetische kernspinresonantie genoemd.

De NMR-methode voor het volgen van het reactief transport in bulksystemen worden geïntroduceerd en beschreven in Hoofdstuk 2. TMOS werd opgelost in n-hexadecaan en geplaatst in buisjes samen met gedemineraliseerd water. Tweedimensionale afbeeldingen werden verkregen van een doorsnede van de buisjes, die een kwalitatief beeld gaven van de massaoverdracht tussen de twee fases. De concentratie van TMOS in olie werd bepaald door het meten van de longitudinale relaxatietijd $T_1$ van waterstof in de oliefase, waarbij gebruik werd gemaakt van calibraties van $T_1$ voor TMOS in n-hexadecaan. Verder werd de transversale relaxatietijd $T_2$ van waterstof in de waterfase gemeten om de voortgang van de gelreactie te volgen. Tijdens de gelreactie neemt de $T_2$ geleidelijk af en bereikt het een minimum (plateau) op het gelpunt. De reductie van $T_2$ wordt veroorzaakt door de interactie van de watermoleculen met de silica-verbindingen en door de vorming van methanol in de gelreactie.

In Hoofdstuk 3 wordt een beeldanalysetechniek gepresenteerd die gebruikt kan worden voor het bepalen van de grensvlakspanning in bulksystemen. De methode is gebaseerd op het volgen van het grensvlak in de NMR-beelden. Een grenswaardeprobleem van de tweede orde, die de grensvlakenergie beschrijft in termen van de grensvlakspanning en van het effect van de zwaartekracht, wordt opgelost en geoïntegreerd voor iedere afbeelding. Zodoende worden de grensvlakspanning bepaald als een functie van de tijd. Bij een initiële concentratie van 40 volumeprocent TMOS in olie is de grensvlakspanning aanvankelijk ongeveer 10 mN m$^{-1}$, maar de spanning neemt geleidelijk toe naar 20 mN m$^{-1}$ als gevolg van de massaoverdracht van TMOS tussen olie en water. Tevens wordt in Hoofdstuk 3 een conceptueel model geïntroduceerd dat de massaoverdracht en hydrolysereactie van TMOS beschrijft en dat is gebaseerd op een partitie-reactie-model.

Het gebruik van een binucleaire NMR-methode voor het karakteriseren van de bulksystemen wordt geïntroduceerd in Hoofdstuk 4. In dit geval werd D$_2$O gebruikt voor de
waterfase. De $T_1$ van waterstof in de oliefase werd gemeten voor de bepaling van de TMOS-concentratie in olie; de $T_2$ van deuterium in de waterfase werd gemeten om de gelreactie te volgen. De experimenten toonden aan dat de $p$H van de waterfase de belangrijkste parameter is die de massaoverdracht- en gelreactiesnelheid bepaalt. De massaoverdracht wordt voornamelijk gedreven door de hydrolysereactie. Bij een neutrale $p$H is de massaoverdracht langzaam maar het wordt versneld in de aanwezigheid van een zure of basische katalysator.

Een fenomenologisch model voor de beschrijving van de condensatiereactie van het gehydrolyseerde TMOS in de tweefasesystemen is gegeven in Hoofdstuk 5. De condensatiereactie wordt beschreven door een populatie-evenwichtsmodel. De verkregen groep differentiaalvergelijkingen werd numeriek opgelost. Het gemiddelde molecuulair gewicht van de populatie ($\bar{M}_w$) divergeert op een bepaalde kritieke tijd $t_c$. Deze tijd neemt af met toenemende hydrolysensnelheid, toenemende condensatiesnelheid of toenemende initiële concentratie van TMOS. Tevens werden de profielen van $\bar{M}_w$ versus tijd gebruikt om een kwalitatieve voorspelling te maken van de $T_2$-profielen uit de experimenten.

**Hoofdstuk 6** behandelt de resultaten van een serie kerninjectieexperimenten. TMOS werd opgelost in olie en geïnjecteerd in zandsteen (Bentheim). Binucleaire NMR metingen werden verricht om het reactief transport binnenin de kern te volgen. Net als in bulk is de massaoverdracht in zandsteen gedomineerd door de hydrolysereactie. Zowel de massaoverdrachtsnelheid als de gelreactiesnelheid zijn afhankelijk van $p$H en temperatuur. Een vergelijkbare trend als in de bulk-systemen werd geobserveerd. De plaatsing en reactie van TMOS in zandsteen bij de onreduceerbare watersaturatie leidt tot een afname van de waterpermeabiliteit die groter is dan de afname van de oliepermeabiliteit.

Een *beam bending*-methode werd gebruikt om het effect te meten van gel op de permeabiliteit van zandsteen. De resultaten werden beschreven in **Hoofdstuk 7**. Metingen aan cilinders van gel toonden aan dat de permeabiliteit van gels, geprepareerd met zure katalysatoren, van de orde 1 nm$^2$ is, wanneer de fractie silica ongeveer 10% is. Gels die geprepareerd zijn met basische katalysatoren vertonen een permeabiliteit tussen 10 en 100 nm$^2$ bij een vergelijkbare concentratie. Wanneer een gelvormende oplossing wordt opgezogen (door capillaire krachten) in een zandsteen, dan leidt de gevormde gel tot een afname van de permeabiliteit van de steen met een factor gelijk aan ongeveer $10^4$.

Tenslotte wordt in **Hoofdstuk 8** een fysisch-mathematisch model gepresenteerd dat het reactief transport van TMOS (of een andere OSC) in poreuze materialen beschrijft. Het model kan gebruikt worden om de plaatsing van TMOS numeriek te simuleren, met betrekking tot zowel lineaire kernen als eenvoudige reservoirs. De gesimuleerde massaoverdrachtsprofielen kwamen goed overeen met de experimentele profielen, met name voor de ongebufferde systemen en de systemen met lage $p$H. In een tweede reeks simulaties werd het TMOS-mengsel continu geïnjecteerd. De drukprofielen worden verklaard door de gemiddelde viscositeit van de olie in de beginfase en door de verandering van de watersaturatie in de latere fases. Het effect van gelvorming, in termen van een toegenomen viscositeit van de waterfase, is niet belangrijk voor de beginfase van het injectieproces.
List of publications

Journal papers

- Pressure dependence of the contact angle in a CO\textsubscript{2} - H\textsubscript{2}O - coal system
  N. Siemons, H. Bruining, H. Castelijns, K.-H. Wolf

- Analysis of coupled mass transfer and sol-gel reaction in a two-phase system
  H. J. Castelijns, H. P. Huinink, L. Pel, P. L. J. Zitha
  *Journal of Applied Physics* 100, 024916/1–9 (2006)

- Characterization of interfacial effects during reactive transport with MRI methods
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- Permeability reduction in porous materials by in situ formed silica gel
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- The effect of pH on coupled mass transfer and sol-gel reaction in a two-phase system
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  *Journal of Physical Chemistry B, accepted* (2007)

- Reactive Transport in Porous Materials revealed by \textsuperscript{1}H and \textsuperscript{2}H Nuclear Magnetic Resonance
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- Investigation of reactive transport phenomena for modification of two-phase flow using NMR
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- Mass transfer and gelation in sandstone cores of a novel water shut-off chemical
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  *paper SPE 99684 presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, U.S.A., April 2006*
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Hein Castelijns was born in Eindhoven, The Netherlands, on January 13, 1979. He attended secondary school (atheneum) at the “Rythovius College” in Eersel from 1991 to 1997. In 2003 Hein obtained a Master’s degree in Applied Physics from the Eindhoven University of Technology. The final work of the Master’s program was about modeling and numerical simulation of atmospheric vortices and transport processes.

The PhD work, which resulted in this dissertation, was performed in the group of Petroleum Engineering from the department of Geotechnology, TU Delft (July 2003 - June 2007). The author worked in close cooperation with the group Transport in Permeable Media of the faculty Applied Physics, TU Eindhoven, where he conducted most of his experimental work. In 2006 he visited the Materials Research group of Professor Scherer at Princeton University for a three-month period.
Prior to the speech, Harald Cramér, member of the Royal Academy of Sciences, addressed the laureates: "Dr. Bloch and Dr. Purcell! You have opened the road to new insight into the micro-world of nuclear physics. Each atom is like a subtle and refined instrument, playing its own faint, magnetic melody, inaudible to human ears. By your methods, this music has been made perceptible, and the characteristic melody of an atom can be used as an identification signal. This is not only an achievement of high intellectual beauty - it also places an analytic method of the highest value in the hands of scientists."

From Les Prix Nobel en 1952, editor Göran Liljestrand, Nobel Foundation, Stockholm, 1953