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Analysis of coupled mass transfer and sol-gel reaction in a two-phase system

H. J. Castelijns  
Department of Geotechnology, Delft University of Technology, Mijnbouwstraat 120, 2628 RX Delft, The Netherlands and Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

H. P. Huinink and L. Pel  
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

P. L. J. Zitha a  
Department of Geotechnology, Delft University of Technology, Mijnbouwstraat 120, 2628 RX Delft, The Netherlands

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The coupled mass transfer and chemical reactions of a gel-forming compound in a two-phase system were studied in detail. Tetra-methyl-ortho-silicate (TMOS) is often used as a precursor in sol-gel chemistry to produce silica gels in aqueous systems. TMOS can also be mixed with many hydrocarbons without chemical reaction, which allows for various applications in multiphase systems. In this study, TMOS was mixed with n-hexadecane and placed together with water in small cylinders. Upon contact of the mixture with the water, TMOS transfers completely to the aqueous phase where it forms a gel through a heterogeneous reaction. Nuclear magnetic resonance imaging and relaxation time measurements were employed to monitor the mass transfer of TMOS from the oleic to the aqueous phase. The longitudinal relaxation time \( T_1 \) was calibrated and used to determine the concentration of TMOS in \( n \)-hexadecane during the transfer. The mass transfer rate was obtained at various temperatures (25–45 °C) and for several initial concentrations of TMOS. In the aqueous phase a sharp decrease in the transversal relaxation time \( T_2 \) is observed which is attributed to the gel reaction, in particular the formation of methanol in the initial stage. The minimum in \( T_2 \) indicates the gelation point, and was found to be strongly dependent on temperature and concentration. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221417]

I. INTRODUCTION

A method to form silica gels commonly applied is the reaction of alkoxy-silanes with water according to the sol-gel principle.\(^1\) 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 proposed by Plazanet and Thomere for consolidation of sand producing formations in oil recovery.\(^2\) The placement and gelation of the chemical in model porous systems were analyzed by Thompson and Fogler.\(^3\) 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.\(^5\)

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,\(^6\) but when TMOS molecules come into contact with water the following hydrolysis reaction takes place:

\[ \text{Si(OCH}_3\text{)}_4 + 4\text{H}_2\text{O} \leftrightarrow \text{Si(OH)}_4 + 4\text{CH}_3\text{OH}. \tag{1} \]

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:

\[ \equiv\text{Si} - \text{OH} + \text{HO} - \equiv \leftrightarrow \equiv\text{Si} - \text{O} - \text{Si} \equiv + \text{H}_2\text{O}. \tag{2} \]

The rate and extent of both reactions are mainly dependent on temperature, \(p\text{H},\) and concentrations.\(^7\) 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 through NMR relaxation time measurements. Dokter et al. studied the gel reaction in alkaline silica solutions which start to gel after adding acid.\(^11\) They observed a minimum in \( T_2 \) near the gel point.\(^9\) NMR measurements of gelling solutions using deuterated TMOS, water, and methanol were carried out by Wonorahardjo et al.\(^12\) The longitudinal relaxation time in the rotating frame \( T_{1p} \) of the solvents showed a transition in decay rate before and after gelation.

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\(^{a)}\)Author to whom correspondence should be addressed; electronic mail: p.l.j.zitha@tudelft.nl
This paper presents the results of a series of experiments as a detailed extension of the previous work. 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 noninvasive, 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 between the components and the contrast in the images is based on the relaxation times \( T_1 \) and \( T_2 \). The times are dependent on the composition of the fluids and temperature. 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. In addition, a semiempirical model is presented. It adequately describes the temperature and concentration dependency of \( T_1 \) for the binary mixtures.

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 measurements are based on the aqueous phase \( T_2 \). During the gel reaction \( T_2 \) decreases and reaches a minimum 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.

II. PRINCIPLE OF NUCLEAR MAGNETIC RELAXATION IN LIQUIDS

In this section we briefly summarize the main mechanisms of nuclear spin relaxation for hydrogen nuclei in pure liquids and binary mixtures.

A. 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. The restoring magnetization is described by an exponential

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

where \( T_1 \) is the overall longitudinal relaxation time. The transversal magnetization \( M_T \) is equal to \( M_z(0) \) 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 transversal relaxation time.

The relaxation processes both for \( T_1 \) and \( T_2 \) are due to intra- and intermolecular interactions of the hydrogen nuclei and to spin-rotational (SR) interactions. The overall relaxation times \( T_{1,2} \) are therefore given by

\[
\frac{1}{T_{1,2}} = \left( \frac{1}{T_{1,2}} \right)_{\text{intra}} + \left( \frac{1}{T_{1,2}} \right)_{\text{inter}} + \left( \frac{1}{T_{1,2}} \right)_{\text{SR}}.
\]

The primary mechanism for intramolecular relaxation is the rotational motion of the molecule. The rotational correlation time \( \tau_r \) is of the order of 1–100 ps, which is often much shorter than the Larmor precession time of the nuclei, so that \( \omega_0 \tau_r \ll 1 \), where \( \omega_0 \) is the Larmor precession frequency. This situation is referred to as the fast motion limit. In this limit \( T_1 = T_2 \), and the intramolecular relaxation rate for a many-nuclei molecule is given by

\[
\left( \frac{1}{T_{1,2}} \right)_{\text{intra}} = \frac{3}{2} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 h^2 \sum_{ij} \frac{1}{r_{ij}} \tau_r,
\]

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 \( j \). Equation (6) 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.

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

\[
\tau_{\text{eff}} = \tau_r \exp \left( \frac{E_A}{RT} \right) + \tau_0,
\]

where \( \tau_r \), \( E_A \), \( R \), \( T \), and \( \tau_0 \) are the inverse frequency factor, the activation energy for rotational motion, the gas constant, the temperature, and an offset, respectively.

The intermolecular contribution is linked to the translational motion of the molecules. With the approximation that all hydrogen nuclei are located at the center of the molecule the relaxivity is expressed as

\[
\left( \frac{1}{T_{1,2}} \right)_{\text{inter}} = \frac{\pi}{5} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 h^2 N_0 \frac{aD}{D},
\]

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. The right-hand side of Eq. (5), therefore, is reduced to the first two terms. From Eqs. (4)–(7) the overall relaxivity for a single-component liquid is given by...
\[ \frac{1}{T_{1,2}} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 H^2 \left[ \frac{1}{n_p} \sum_{j=1}^{n_p} \frac{1}{\rho_j} c_{\text{eff}, \rho_j} \right] \left( \frac{\pi N_0}{5 aD} \right). \]  

Although in the fast motion limit the transversal 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 \( T_1 \).

### B. Binary mixtures

In a mixture of liquids A and B, there is an additional intermolecular contribution that is 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 of Eq. (9) by

\[ \frac{1}{T_{1,2}^A} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 H^2 c_A \left[ \frac{1}{\rho} c_{\text{eff}, \rho} + \frac{\pi N_0}{5 aD} \right] \left( \frac{N_0 A}{D_{AA}} + \frac{N_0 B}{D_{AB}} \right), \]

\[ \frac{1}{T_{1,2}^B} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 H^2 c_B \left[ \frac{1}{\rho} c_{\text{eff}, \rho} + \frac{\pi N_0}{5 aD} \right] \left( \frac{N_0 A}{D_{BA}} + \frac{N_0 B}{D_{BB}} \right), \]

where \( c_A \) and \( c_B \) are constants related to the molecular structures and \( D_{ij} \) are the mutual diffusion coefficients. Suppose that 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 biexponential relaxation behavior as described by

\[ M_z(t) = M_0 \left[ 1 - f \exp \left( -\frac{t}{T_1^A} \right) - (1 - f) \exp \left( -\frac{t}{T_1^B} \right) \right]. \]

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, \( M_2 \) relaxes according to a single exponential as defined by Eq. (3). Similarly, the transversal magnetization of the mixture relaxes back to zero after application of the 90° pulse according to the biexponential function

\[ M_\perp(t) = M_0 \left[ f \exp \left( -\frac{t}{T_2^A} \right) + (1 - f) \exp \left( -\frac{t}{T_2^B} \right) \right]. \]

Both Eqs. (12) and (13) can easily be extended to describe the multieponential relaxation in multicomponent mixtures.

### III. EXPERIMENT

#### A. Chemicals and preparation

Tetra-methyl-ortho-silicate, Si(OCH₃)₄, was obtained from Aldrich (>99% pure). For the oleic phase, \( n \)-hexadecane or \( n \)-C\text{\textsubscript{16}}H\text{\textsubscript{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. For the aqueous phase we used double-deionized water.

Several gel samples were prepared with demineralized water and TMOS in different volume ratios and at ambient conditions. The initial volume fraction \( \delta^v_0 \) (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 was formed. It was observed that after several weeks the high-concentration gels showed a small degree of syneresis.

#### B. NMR apparatus and sequences

Relaxation times and \( T_1 \)-weighted images of the samples were recorded with a 4.7 T NMR spectrometer operating at a frequency of 200 MHz for \(^1\)H. The setup consists of a superconducting magnet (Oxford Instruments, Oxon, UK) with a vertical, narrow-bore insert (Doty, Columbia, USA) with an inner diameter of 40 mm. The insert has 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 \( 22 \pm 2 \) °C. However, for the experiments 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. The fluid is invisible to the NMR setup, and the temperature can be controlled between 10 and 65 °C with an accuracy of about 1 °C.

Two-dimensional (2D) images were obtained with a turbo spin echo (TSE) sequence. A schematic view of the sequence is shown in Fig. 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 a readout gradient. Self-diffusion coefficients were measured with the pulsed field gradient (PFG) diffusion sequence, which is similar to the imaging sequence; however, two extra gradient pulses are applied before and after the 180° rf pulse to attenuate the signal.
The longitudinal relaxation time $T_1$ of each sample was measured by a one-dimensional (1D) saturation recovery sequence.\textsuperscript{23} With this method the longitudinal magnetization $M_z$ of the sample is destroyed by applying a train of rf pulses of random lengths and with random intervals. Subsequently, the magnetization is restored 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\textsuperscript{13,14} in which a spin echo train is acquired by applying a 90°–($\tau$–180°) sequence of rf pulses, where $\tau$ is the interecho time $\Delta T_E$. In this sequence the readout 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 and the use of pulsed gradients, similar to the PFG method. For a single-component system the apparent $T_2$ can be expressed by

$$T_{2,\text{apparent}} = \left( \frac{1}{T_2} + \frac{bD}{\Delta T_E} \right)^{-1},$$

where $b$ is a diffusion weighting factor that depends on the timing, shape, and strength of the gradients used. With respect to the readout gradient the $b$ factor is approximately equal to $(\gamma G \delta t/2)^2$, where $G$ is the gradient strength and $\delta t$ is the duration of the readout. The interecho time and the duration of the readout were constantly taken as 7.2 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 (Ref. 24) to give quasi-continuous $T_2$ spectra, consisting of a hundred points on a logarithmic $T_2$ axis. The numerical inversion of the echo trains involves an inverse Laplace transform which is inherently an ill-posed problem. The routine contains a regularization procedure which is required in order to obtain a stable solution, and results in a smoothing of the spectra. 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° and 180° conditions of the rf pulses are therefore needed.

C. 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). The initial volume fractions of TMOS in n-hexadecane were 0.20 and 0.40, respectively, for each temperature considered. After injection, the samples were quickly placed in the NMR setup. Subsequently, a continuous loop of NMR measuring sequences was executed: a $T_1$ measurement using the saturation recovery sequence, a 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 readout gradient (50, 100, and 200 mT/m).

For every sequence the readout gradient was set in the vertical direction. Slice selection was applied perpendicularly to the readout direction, yielding a slice thickness of about 4 mm. The variation of the gradient strength in the CPMG measurements and the constant readout duration result in a varying resolution of the 1D profiles. Nevertheless, the liquid phases are easily reconstructed and identified from the profiles. The magnetic susceptibilities of water and $n$-hexadecane are $-9.0 \times 10^{-6}$ and $-8.0 \times 10^{-6}$, respectively.\textsuperscript{25} At 4.7 T the resulting frequency mismatch is about 200 Hz. With respect to the applied readout 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 min, so that the loop time is about 15 min.

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 min, 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 min.

IV. RESULTS AND DISCUSSION

A. Calibration results

1. TMOS/n-hexadecane mixtures

The saturation recovery data of the TMOS/n-hexadecane mixtures were evaluated by fitting monoexponential and biexponential decay curves, as given by Eqs. (3) and (12), respectively. For each concentration and temperature the decay appeared to be virtually monoexponential, and a robust biexponential fit could not be obtained. The individual $T_1$'s for TMOS and $n$-hexadecane in the mixtures are relatively close. The noise present in the spin echo data results in significant errors in the fit parameters when applying a multieponential fit even at high signal-to-noise ratios. Especially for intermediate concentrations the slight deviation from monoexponential behavior causes the monoexponential 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 $T_1$ measurements were found to be within 5%. The results are shown in Fig. 2. For $n$-hexadecane $T_1$ is 0.763 s at 20.2 °C and increases to 1.69 s at 66.7 °C. For pure TMOS $T_1$ is 3.52 s at 21.2 °C and increases to 4.14 s at 66.3 °C. In general, $T_1$ increases monotonically with con-
The comparison is shown in Fig. 3 for \( T = 20 \) °C and \( T = 40 \) °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.

2. 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 II the results are summarized together with \( T_1 \) and \( T_2 \) for water, methanol, and TMOS, which are substances involved in the sol-gel reaction. The longitudinal relaxation in the gels appeared to be monoexponential. For the lowest initial concentration of TMOS (\( \phi = 0.05 \)), \( T_1 \) is almost equal to that of water, but decreases with increasing concentration. Between \( \phi = 0.30 \) and \( \phi = 0.50 \), \( T_1 \) is constant (about 1.70 s).

The CPMG data was analyzed using the inversion routine CONTIN. The gel \( T_2 \) spectra showed a multieponential behavior with well-separated components within the range of the inversion. Additionally, a discrete triexponential fit was performed on the spin echo trains to quantify the exponents. A dominant component was found on the order of tens of milliseconds for each gel that appeared to be almost independent on the readout gradient used, so that the \( T_2 \) is not influenced by molecular diffusion. Between \( \phi = 0.25 \) and \( \phi = 0.50 \), \( T_2 \) is almost constant (about 30 ms).

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

![Diagram](image_url)

**FIG. 2.** 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 \( T_1 \).

![Diagram](image_url)

**FIG. 3.** Relaxation time \( T_1 \) of TMOS/n-hexadecane mixtures as a function of concentration after interpolation of the experimental data for different temperatures. The predicted \( T_1 \) is shown as well.

<table>
<thead>
<tr>
<th>( n )-hexadecane</th>
<th>TMOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau' ) (ps)</td>
<td>0.0422</td>
</tr>
<tr>
<td>( E_a ) (1 mol(^{-1}))</td>
<td>15.468</td>
</tr>
<tr>
<td>( \tau_0 ) (ps)</td>
<td>1.70</td>
</tr>
<tr>
<td>( \tau_{c, eff} ) (ps) at ( 20 ) °C</td>
<td>25.8</td>
</tr>
</tbody>
</table>

**TABLE I.** Fitting parameters for the relaxation time model of the pure liquids.
from the initial water/TMOS ratio. This is denoted as the equivalent ratio $R_{eq}$ and is given in Table II 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. At the molecular scale the mixing of methanol with water is incomplete, leading to complex solution structures. This is due to the chainlike and ringlike alignment of the methanol molecules surrounding the water molecules. The structure is caused by hydrogen bonds, on the one hand, and repulsion between the methyl groups and water, on the other. Additionally, a rapid exchange between 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 Fig. 4. Water shows a peak near $T_2 = 1.66$ s. Methanol has a bimodal distribution, which is attributed to the different relaxation modes of the methyl group protons and the hydroxyl protons. The area of the peaks indicates the relative proton density of the species. 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 degree of hydrogen exchange between the 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. $T_1$ and $T_2$ for water/methanol mixtures of various ratios are listed in Table II.

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 the interaction of the liquids with the silica surface, respectively. See, for example, Liu et al. and Korb et al.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$R$</th>
<th>$T_1$ (s)</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>3.26</td>
<td>1.66</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>TMOS</td>
<td>3.57</td>
<td></td>
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<td></td>
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<tr>
<td>methanol</td>
<td>4.09</td>
<td></td>
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<td>Water-methanol</td>
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<tr>
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<td>0.027</td>
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<tr>
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<td>0.026</td>
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</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>
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FIG. 4. $T_2$ spectra measured at 25 °C of water, methanol, and a mixture of 50 vol % methanol in water.
B. Two-phase bulk systems

1. 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 phases are always clearly separated due to the contrast in $T_1$ (see Fig. 5). 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 have a significant increase in intensity. The images further reveal that during the experiment the interface gradually moves upward, so that the phase volumes change, indicating the mass transfer of TMOS from one phase to another. 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 h), 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.

2. 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 Fig. 6. At each time step the profile consists of two plateaus separating the oleic from the aqueous phase. Similar 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 cannot therefore 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 Figs. 7 and 8. 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 h. The experiments with initial concentration of 0.20 show a similar trend, but the mass transfer is complete after about 10 h. A sharp indication is not possible due to the gradual transition. The concentration profiles show an exponential decay; therefore the concentration data was 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 III. For the initial concentration of 20 vol% TMOS in n-hexadecane the mass transfer rate is about 0.5 h$^{-1}$ and does not depend significantly on temperature. The 40 vol% experiments have
higher transfer rates of at least 1.0 h⁻¹, which are also increasing with temperature.

3. Relaxation of the aqueous phase

With respect to the aqueous phase $T_1$ was not analyzed further. Instead, the CPMG data was analyzed in detail. For each experiment the data was 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 for each echo in the spin echo train. The $T_2$ spectra as a function of time are shown in Fig. 9 for one of the experiments, but all experiments showed a similar trend. A dominant component is initially found near the $T_2$ for water but rapidly moves to shorter times. 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 reaches a minimum after several hours. 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. $^{11}$

The spectra inherently produce Gaussian-like peaks; therefore the dominant component was fitted with a Gaussian in order to quantify its position on the $T_2$ axis. A detail of the resulting fit is shown in Fig. 10. Like the calibration samples the $T_2$ is virtually independent of gradient strength. The final $T_2$ is slightly longer (at 25 °C) than the values obtained from the calibration samples. This is attributed to aging effects.

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 to find the points at which the minima are found. The resulting minimum time (with an accuracy of about 30 min) was subsequently compared to the gel times obtained from the tilting test tube experiments (as demonstrated in Fig. 11). A good agreement is found between the gel times and the minimum $T_2$ times. The minimum in $T_2$ therefore appears to be an adequate measure for the gel time in these experiments.

### Table III

Overall mass transfer coefficient $\kappa$ (h⁻¹) of the two-phase bulk experiments. $\phi_0$ is the initial TMOS volume concentration.

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

FIG. 8. Average concentration of TMOS in the oleic phase as a function of time for different temperatures. The initial TMOS concentration is 0.20.

FIG. 9. $T_2$ spectra of the aqueous phase (averaged) as a function of 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.

FIG. 10. Details of dominant $T_2$ component in the aqueous phase as a function of time for the experiment with initial TMOS fraction of 0.4 and temperature of 25 °C. The $T_2$ was measured using three different readout gradient strengths as indicated in the legend. The lines in the graph indicate the construction used to find the time at which the $T_2$ becomes constant during the experiment.
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 in $T_2$, which appears after several hours when the fluids are brought into contact. The gel time decreases with increasing temperature and with increasing initial TMOS concentration.

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