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

Citation for published version (APA):

Castelijns, H. J., Huinink, H. P., Pel, L., & Zitha, P. L. J. (2006). Analysis of coupled mass transfer and sol-gel reaction in a two-phase system. *Journal of Applied Physics*, 100(2), 024916-1/9. [024916].
<https://doi.org/10.1063/1.2221417>

DOI:

[10.1063/1.2221417](https://doi.org/10.1063/1.2221417)

Document status and date:

Published: 01/01/2006

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

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

(Received 3 January 2006; accepted 3 June 2006; published online 27 July 2006)

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.^{3,4} 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,^{1,6} but when TMOS molecules come into contact with water the following hydrolysis reaction takes place:

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:

The rate and extent of both reactions are mainly dependent on temperature, pH, and concentrations.^{1,7–10} 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. ²H-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 $T_{1\rho}$ of the solvents showed a transition in decay rate before and after gelation.

^{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.⁵ 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 nonintrusive, 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

$$M_z(t) = M_z(0) \left[1 - \exp\left(-\frac{t}{T_1}\right) \right], \quad (3)$$

where T_1 is the overall longitudinal relaxation time.^{13,14} The transversal 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

$$M_T(t) = M_T(0) \exp\left(-\frac{t}{T_2}\right), \quad (4)$$

where T_2 is the transversal relaxation time.^{13,14}

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.^{15,16} The overall relaxation times $T_{1,2}$ are therefore given by

$$\frac{1}{T_{1,2}} = \left(\frac{1}{T_{1,2}}\right)_{\text{intra}} + \left(\frac{1}{T_{1,2}}\right)_{\text{inter}} + \left(\frac{1}{T_{1,2}}\right)_{\text{SR}}. \quad (5)$$

The primary mechanism for intramolecular relaxation is the rotational motion of the molecule. The rotational correlation time τ_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 ω_0 is the Larmor precession frequency. This situation is referred to as the *fast motion limit*.¹³ In this limit $T_1 = T_2$, and the intramolecular relaxation rate for a many-nuclei molecule is given by¹⁷

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

where μ_0 , γ , $\hbar$, 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.¹⁸

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

$$\tau_{c,\text{eff}} = \tau' \exp\left(\frac{E_A}{RT}\right) + \tau_0, \quad (7)$$

where τ' , E_A , R , T , and τ_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^{13,19}

$$\left(\frac{1}{T_{1,2}}\right)_{\text{inter}} = \frac{\pi}{5} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 \frac{N_0}{aD}, \quad (8)$$

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.²⁰ 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

$$\frac{1}{T_{1,2}} = \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \left(\frac{3}{n_p} \sum_{i>j} \frac{1}{r_{ij}^6} \tau_{c,\text{eff}} + \frac{\pi N_0}{5 aD} \right). \quad (9)$$

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

$$\frac{1}{T_{1,2}^A} = \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \left[c_A \tau_{c,\text{eff},A} + \frac{\pi}{5a_A} \left(\frac{N_{0A}}{D_{AA}} + \frac{N_{0B}}{D_{AB}} \right) \right], \quad (10)$$

$$\frac{1}{T_{1,2}^B} = \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \left[c_B \tau_{c,\text{eff},B} + \frac{\pi}{5a_B} \left(\frac{N_{0A}}{D_{BA}} + \frac{N_{0B}}{D_{BB}} \right) \right], \quad (11)$$

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

$$M_z(t) = M_0 \left[1 - f \exp\left(-\frac{t}{T_1^A}\right) - (1-f) \exp\left(-\frac{t}{T_1^B}\right) \right], \quad (12)$$

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. (3). Similarly, the transversal magnetization of the mixture relaxes back to zero after application of the 90° pulse according to the biexponential function

$$M_T(t) = M_0 \left[f \exp\left(-\frac{t}{T_2^A}\right) + (1-f) \exp\left(-\frac{t}{T_2^B}\right) \right]. \quad (13)$$

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

III. EXPERIMENT

A. Chemicals and preparation

Tetra-methyl-ortho-silicate, $\text{Si}(\text{OCH}_3)_4$, was obtained from Aldrich (>99% pure). For the oleic phase, *n*-hexadecane or *n*- $\text{C}_{16}\text{H}_{34}$ (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. For the aqueous phase we used double-demineralized water.

Several gel samples were prepared with demineralized water and TMOS in different volume ratios and at ambient

FIG. 1. Schematic representation of the 2D turbo spin echo sequence. After the initial 90° rf pulse the 180° rf pulse and the subsequent readout of the echo are repeated N times, during which the phase-encoding gradient is varied. In this example $N=2$.

conditions. The initial volume fraction ϕ_T^g (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 ^1H . 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 $22 \pm 2^\circ\text{C}$. 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° .

Two-dimensional (2D) images were obtained with a *turbo spin echo* (TSE) sequence.²¹ 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,²² 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.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,^{13,14} in which a spin echo train is acquired by applying a $90^\circ - (\tau - 180^\circ)_n$ sequence of rf pulses, where 2τ is the interecho time $\Delta\tau_E$. 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

$$T_{2,\text{apparent}} = \left(\frac{1}{T_2} + \frac{bD}{\Delta\tau_E} \right)^{-1}, \quad (14)$$

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 $(\gamma G \delta / 2)^2$, where G is the gradient strength and δ 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 quasicontinuous 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 -9.0×10^{-6} and -8.0×10^{-6} , respectively.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 multiexponential 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-

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 .

centration and with temperature. The calibrations are used to determine the concentration of TMOS in *n*-hexadecane in the two-phase bulk experiments.

Next, the experimental results are evaluated with the model equations for the relaxation. The intermolecular contribution to the relaxation in Eqs. (10) and (11) is predicted first. The number of protons N_{0A} and N_{0B} is derived from the concentration of TMOS in *n*-hexadecane. The radius of approach a is 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. However, for all coefficients D_{ij} the average self-diffusion coefficient of the mixture is used. This was measured with the PFG method, which seems acceptable given the value of the self-diffusion coefficient for the pure liquids (i.e., $1.59 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for TMOS and $0.40 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for *n*-hexadecane at 25 °C).

The intramolecular part of the relaxation contains the effective correlation time $\tau_{c,\text{eff}}$ which is found by an optimization process as follows. Here $\tau_{c,\text{eff}}$ as defined in Eq. (7) is assumed to be independent of concentration; therefore the term is derived from the experimental data of pure TMOS and pure *n*-hexadecane. The predicted intermolecular term is subtracted from the experimental, total T_1 for each temperature. Then the remainder is fitted as a function of temperature with Eqs. (6) and (7). 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 , τ' , and τ_0 , are shown in Fig. 2 as the solid lines. 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. (10) and (11)] using the obtained fitting parameters (Table I). The saturation recovery decay is subsequently constructed as given by Eq. (12), and the result is fitted with the monoexponential decay function in order to compare the calculated values to the experimental results. The comparison is shown in Fig. 3 for $T=20^\circ\text{C}$ and T

TABLE I. Fitting parameters for the relaxation time model of the pure liquids.

	<i>n</i> -hexadecane	TMOS
τ' (ps)	0.0422	0.000 41
E_A (J mol ⁻¹)	15 468	18 497
τ_0 (ps)	1.70	3.66
$\tau_{c,\text{eff}}$ (ps) at 20 °C	25.8	4.47

$=40^\circ\text{C}$. 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.

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 ($\phi_T^0=0.05$), T_1 is almost equal to that of water, but decreases with increasing concentration. Between $\phi_T^0=0.30$ and $\phi_T^0=0.50$, 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 multiexponential 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 $\phi_T^0=0.25$ and $\phi_T^0=0.50$ 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

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 II. Results of the NMR calibration measurements for the gels (at $T=22\pm 2$ °C) and liquids (at $T=25\pm 1$ °C). T_2 was measured with an interecho time of 7.2 ms and with a pulsed readout gradient $G=100$ mT/m. ϕ_T^g 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.

Substance	R	T_1 (s)	T_2 (s) Exponent		
			First	Second	Third
Water		3.26	1.66		
TMOS		3.57	1.33		
methanol		4.09		0.42	1.16
Water-methanol	8.97	2.54	0.195	...	1.38
	3.36	2.29	0.141	...	1.59
	2.24	2.32	0.070	0.70	1.54
	1.49	2.47	0.060	0.73	1.40
	0.56	2.95	0.055	0.46	1.28
Gel (ϕ_T^g)	R_{eq}				
0.05	38.6	2.71	0.120	0.25	0.50
0.10	18.0	2.34	0.065	0.18	0.53
0.15	11.2	2.15	0.045	0.24	0.58
0.20	7.7	2.03	0.038	0.31	0.62
0.25	5.7	1.90	0.029	0.30	0.66
0.35	3.3	1.70	0.027	0.22	0.66
0.40	2.6	1.69	0.026	0.29	0.64
0.50	1.6	1.70	0.029	0.32	0.66

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.²⁶ 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.²⁷ 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.*²⁸ and Korb *et al.*²⁹

FIG. 4. T_2 spectra measured at 25 °C of water, methanol, and a mixture of 50 vol % methanol in water.

FIG. 5. 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 ($\phi_T=0.40$), and the lower phase is demineralized water. (Left) First frame at $t=8$ min after injection. (Right) Final frame after 14.5 h.

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 also 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

FIG. 6. 1D T_1 profiles of bulk system in the vertical direction. The phases are separated through a sharp contrast in T_1 . 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.

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.,

$$\phi(t) = \phi_0 \exp(-\kappa t), \quad (15)$$

where κ 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

FIG. 7. Average concentration of TMOS in the oleic phase as a function of time for different temperatures. The initial TMOS concentration is 0.40.

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.

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. This was done by averaging the part of the 1D signal profiles related to 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

TABLE III. Overall mass transfer coefficient κ (h^{-1}) of the two-phase bulk experiments. ϕ_0 is the initial TMOS volume concentration.

Temperature ($^{\circ}\text{C}$)	$\phi_0=0.20$	$\phi_0=0.40$
25	0.44 ± 0.02	1.02 ± 0.04
35	0.46 ± 0.03	1.14 ± 0.04
45	0.43 ± 0.01	1.52 ± 0.09

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.

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.

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.

FIG. 11. 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.

V. 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 nonintrusive manner.

The prepared gels showed a significant decrease in the transversal 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 are attributed to methanol. The shortening of the water T_2 component is due to the interaction of water and 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 phases 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 into 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 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.

ACKNOWLEDGMENTS

This research was supported by the Dutch Technology Foundation (STW) through Project No. DAR 5756. Additional support was provided by Shell, INA Naftaplin, Chevron, Statoil, Conoco-Philips, and Gaz de France.

- ¹C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic, New York, 1990).
- ²V. Plazanet and R. Thomere, Institut National de la Propriété Industrielle (Paris) Patent No. 2,624,198 (June 9, 1989).
- ³K. E. Thompson and H. S. Fogler, SPEJ **2**, 350 (1997).
- ⁴K. E. Thompson and H. S. Fogler, Phys. Rev. E **57**, 5825 (1998).
- ⁵H. J. Castelijns, L. Pel, H. P. Huinink, and P. L. J. Zitha, Proceedings of the SPE Sixth European Formation Damage Conference, Scheveningen, The Netherlands, May 25–27, 2005, Paper SPE 94559.
- ⁶R. K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).
- ⁷H. Schmidt, H. Scholze, and A. Kaiser, J. Non-Cryst. Solids **63**, 1 (1984).
- ⁸J. C. Pouxviel, J. P. Boilot, J. C. Beloeil, and J. Y. Lallemand, J. Non-Cryst. Solids **89**, 345 (1987).
- ⁹R. A. Assink and B. D. Kay, J. Non-Cryst. Solids **99**, 359 (1988).
- ¹⁰O. K. Filho and M. A. Aegerter, J. Non-Cryst. Solids **105**, 191 (1988).
- ¹¹W. H. Dokter, H. F. V. Garderen, T. P. M. Beelen, J. W. D. Haan, L. J. M. V. D. Ven, and R. A. V. Santen, Colloids Surf., A **72**, 165 (1993).
- ¹²S. Wonorahardjo, G. E. Ball, J. Hook, and G. Moran, J. Non-Cryst. Solids **271**, 137 (2000).
- ¹³B. Cowan, *Nuclear Magnetic Resonance and Relaxation* (Cambridge University Press, Cambridge, England, 1997).
- ¹⁴P. T. Callaghan, *Principles of Nuclear Magnetic Resonance Microscopy* (Oxford Science, New York, 1991).
- ¹⁵N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
- ¹⁶A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).
- ¹⁷J. G. Powles and D. J. Neale, Proc. Phys. Soc. London **78**, 377 (1961).
- ¹⁸H. G. Hertz, Prog. Nucl. Magn. Reson. Spectrosc. **16**, 115 (1983).
- ¹⁹P. S. Hubbard, Phys. Rev. **131**, 275 (1963).
- ²⁰P. S. Hubbard, Phys. Rev. **131**, 1155 (1963).
- ²¹M. T. Vlaardingerbroek and J. A. Boer, *Magnetic Resonance Imaging: Theory and Practice* (Springer-Verlag, New York, 1997).
- ²²E. O. Stejskal and J. E. Tanner, J. Chem. Phys. **42**, 288 (1965).
- ²³B. Blümich, *NMR Imaging of Materials* (Clarendon, Oxford, 2000).
- ²⁴S. W. Provencher, Comput. Phys. Commun. **27**, 213 (1982).
- ²⁵D. R. Lide, *Handbook of Chemistry and Physics* (CRC, Boca Raton, FL, 2003).
- ²⁶F. Giro, M. F. Goncalves, A. G. M. Ferreira, and I. M. A. Fonseca, Fluid Phase Equilib. **204**, 217 (2003).
- ²⁷J. H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J. E. Rubensson, D. K. Shuh, H. Agren, and J. Nordgren, Phys. Rev. Lett. **91**, 157401 (2003).
- ²⁸G. Liu, Y. Li, and J. Jonas, J. Chem. Phys. **95**, 6892 (1991).
- ²⁹J. P. Korb, A. Delville, S. Xu, G. Demeulenaere, P. Costa, and J. Jonas, J. Chem. Phys. **101**, 7074 (1994).