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Measurement of Dilute ^{29}Si Species in Solution Using a Large Volume Coil and DEFT NMR

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A large-sample-volume nuclear magnetic resonance (NMR) spectroscopy probehead has been developed for the detection and characterization of low concentrations of ^{29}Si species in aqueous solution. The approach described entails the use of a large-diameter radio frequency solenoid coil that permits substantially larger sample volumes to be investigated at moderate magnetic field strengths, compared with conventional NMR probehead configurations. In addition, difficulties presented by long ^{29}Si T_1 relaxation times have been circumvented by using the DEFT NMR pulse sequence, which permits more rapid signal averaging. Through a combination of these hardware and methodological improvements, high-resolution ^{29}Si NMR spectra have been obtained at 4.2 T (^{29}Si resonance frequency = 36.8 MHz) for an 800 μM solution of 96% ^{29}Si-enriched silicic acid, H_4SiO_4 (pH ≈ 8), with a signal-to-noise ratio of 16 and a line width of 31 Hz after 3 h of total measurement time.

In biological systems, silicon has often been regarded as a difficult nucleus for study by solution-state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy for a number of reasons: the natural abundance of the NMR-active isotope, ^{29}Si, is low (4.7%); enriching samples (when possible) is generally expensive; aqueous ^{29}Si species typically have long spin−lattice (T_1) relaxation times; and soluble silicon species are typically found in low concentrations in biological systems.[1] Additional complications in solution-state ^{29}Si detection by NMR arise in those systems in which silicon species participate in transient kinetic processes during the NMR experiment. In such cases, measurements represent time averages that may be limited by ^{29}Si signal sensitivity. Long T_1 relaxation times are typical in both solution- and solid-state ^{29}Si NMR and result from relatively inefficient coupling between the magnetic moments of ^{29}Si nuclei and the motional (e.g., translational, rotational, etc.) modes of their associated molecules.[2,3] For samples requiring signal averaging for improved sensitivity, long relaxation times often necessitate the use of long delay times to allow the ^{29}Si spin system to reestablish thermal equilibrium after the perturbation caused by radio frequency excitation.

Recently, Kinrade and Knight[4] demonstrated sensitivity improvements for measuring dilute ^{29}Si species in solution using the DEPT (distortionless enhanced polarization transfer) NMR experiment in a 17.6 T magnetic field. They were able to measure 1 ppm (mass basis) total silicon in a sample of hexamethyldisiloxane (containing a natural abundance mixture of Si isotopes) in chloroform after 13 h with a signal-to-noise ratio of 7 using a standard 10-mm-diameter NMR tube (with a functional volume of approximately 3 cm^3). To ameliorate the problem of long ^{29}Si relaxation times, the DEPT NMR pulse sequence was used to transfer polarization from abundant, high-gyromagnetic-ratio hydrogen nuclei to covalently bound ^{29}Si nuclei via scalar (J) couplings.[5−7] Because scalar ^{29}Si-^{1}H couplings persist for rapidly and isotropically mobile species, this strategy is effective in the solution state and can enhance the ^{29}Si NMR signal by a factor of approximately 5 compared to single-pulse ^{29}Si excitation. In addition, under such conditions, the relevant relaxation behavior is that of the hydrogen nuclei, whose T_1 values are usually much shorter than those of ^{29}Si species, thus allowing more rapid signal averaging.[3] This approach, however, is limited to systems that contain ^{29}Si nuclei that are scalar-coupled to ^{1}H nuclei—a condition that will not generally exist in aqueous silicate solutions, where rapid proton exchange dynamics often prevail.

Here, we present an improved methodology for detecting low liquid-phase concentrations of ^{29}Si species, including dilute aqueous silicate solutions. A central feature is the use of a large-diameter solenoid coil that allows high-resolution ^{29}Si NMR spectra to be obtained from a large sample volume (approximately 27 cm^3). This provides an order of magnitude increase in the number of detectable spins in the sample, compared with conventional NMR coil configurations. In addition, to overcome difficulties presented by long ^{29}Si T_1 relaxation times, we have employed the DEFT NMR experiment (driven equilibrium Fourier transform),[8−11] which is described in more detail below.

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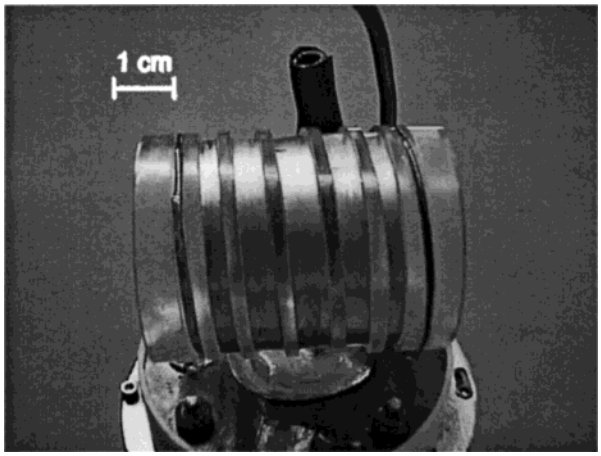

Figure 1. The large-diameter NMR coil/probehead used to obtain increased ^{29}Si signal sensitivity with high resolution in solution-state ^{29}Si NMR spectra. The 7-turn coil is 4.7 cm long and consists of a copper ribbon wound on a polymeric (Lexan) mount with an inner diameter of 31 cm. The copper ribbon has variable width (see Figure 2), which allows a higher turn density at the ends, to improve spectral resolution. The sample volume within the coil is approximately 27 cm^3.

EXPERIMENTAL SECTION

Silicate Solution Preparation. All chemicals were used as received from Aldrich Chemicals, Inc. (Milwaukee, Wisconsin), unless otherwise stated. Two silicate solutions were prepared, which bracket the ^{29}Si NMR spectral region in which most aqueous silicate species are observed: one, a dilute aqueous sodium silicate (Na_2SiO_3) solution (800 μM), which corresponds to concentrations of dissolved silica relevant to biological systems,[12] and a second alkaline (pH > 13.0) silicate solution containing exclusively double-four-ring (D4R) oligomeric silicate anions (natural abundance ^{29}Si, ~0.9 M D4R, as described elsewhere[13]). The dilute sodium silicate solution was prepared by heating 95.65% ^{29}Si-enriched SiO_2 (purchased from Oak Ridge National Laboratory) with sodium carbonate in a platinum crucible to 3000 °C. The sodium silicate was subsequently dissolved in Nanopure water to obtain a highly ^{29}Si-enriched solution of silicic acid. The pH of this solution was adjusted to a value of pH 8. Visual inspection of the solution showed neither cloudiness nor the presence of solid precipitates, consistent with NMR characterization experiments (see below).

Solution-State ^{29}Si NMR: Probehead and Pulse Sequence. All solution-state ^{29}Si NMR spectra were obtained on a Chemagnetics CMX-180 spectrometer operating at a ^{29}Si frequency of 36.8 MHz with an 89-mm wide-bore 4.2 T superconducting magnet. All spectra are referenced to the ^{29}Si signal from tetramethylsilane (TMS).

Figure 1 shows a photograph of the large-diameter NMR coil and probehead used for measuring large-volume samples of dilute silicate solutions. The coil has a length of 4.7 cm, a diameter of 3.1 cm, and 7 turns. In addition to the size of the coil, an important characteristic is its nonuniform winding pattern. To overcome excitation difficulties due to radio frequency (rf) field inhomogeneities, we have employed a strategy developed by Privalov et al.,[14] which uses a ribbon conductor of variable width and constant (and small, 2 to 3 mm) interturn spacing. This approach allows for a continuously variable pitch along the length of the coil. As a consequence, the coil has a higher turn density at the ends, which ensures that the $\boldsymbol{B}_1$ magnetic field (produced by each rf pulse) does not decrease excessively along the axial direction. The small interturn spacing meanwhile minimizes field inhomogeneities in the radial direction. This results in a highly uniform $\boldsymbol{B}_1$ field up to within a few millimeters of the ends of the large coil. Furthermore, at each coil end, the $\boldsymbol{B}_1$ field is approximately 75% of the $\boldsymbol{B}_1$ field measured at the axial coil center; for comparison, this value is typically 50% for a standard solenoid coil design.

The large-diameter coil was designed using a *Mathematica* algorithm[14] that assumes a uniform current distribution in the conductor to generate the proper coil shape. The input parameters for the program were the radius and length of the coil, the number of turns, the interturn gap width, and an adjustable parameter, a, that describes the degree to which the conductor width varies along the coil. With $a = 0$, the conductor has a constant width along the coil axis (corresponding to a standard solenoid coil); for $a < 0$, the width decreases with the axial distance from the coil center, while for $a > 0$ the width increases. A value of $a = -0.015$ was used in the present case, which yields an easily constructed coil with properties and performance that lead to improved sensitivity and resolution for large-volume samples. Upon parametrization of the coil shape, the program calculates the magnetic field at several discrete points within the volume of the coil by numerically integrating the Biot-Savart Law[15]

$$\boldsymbol{B} = (\mu_0 I/4\pi)(\boldsymbol{l} \times \boldsymbol{r})/r^3 \qquad (1)$$

where $\boldsymbol{B}$ is the magnetic field vector, $\boldsymbol{l}$ is the length vector along the conductor tangential to the cylinder, $\boldsymbol{r}$ is the radial position vector, I is the current in the conductor, and the other symbols have their usual meanings. The program can be used to optimize the homogeneity of the calculated rf field. In addition to providing a three-dimensional field profile within the coil, the program also generates a plot (Figure 2) of the conductor shape when the coil is extended. When scaled properly, the plot can be used to pattern a strip of copper tape from which the correctly shaped coil conductor may be cut. The shaped copper ribbon is then wound onto a grooved polymeric coil mount, such that the polymer provides electrical isolation between adjacent turns. Lexan (polycarbonate, GE Plastics) was used in the present case, as it produced an optically clear coil mount, is easier to machine, and has slightly better dielectric loss properties than Plexiglas (poly(methyl methacrylate), Rohm and Haas).

For systems with long T_1 relaxation times, such as ^{29}Si species in aqueous solutions, use of the DEFT NMR pulse sequence allows for more rapid signal averaging, and therefore, superior

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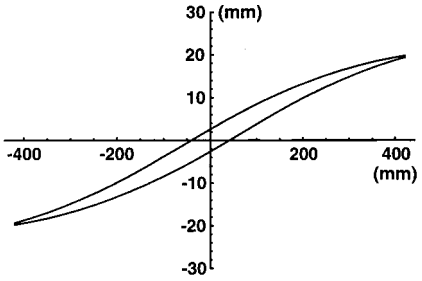

Figure 2. Conductor configuration for winding a large-diameter NMR coil to provide a homogeneous $\boldsymbol{B}_1$-field during the application of radio frequency pulses. Axis units are in millimeters. The degree to which the conductor width varies along the coil axis corresponds to a taper parameter $a = -0.015$ (see text).

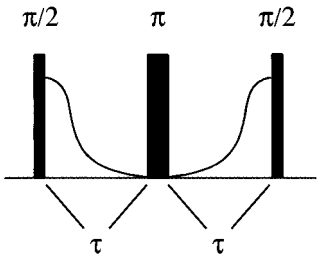

Figure 3. Schematic diagram of the DEFT NMR pulse sequence for overcoming long solution-state ^{29}Si spin−lattice relaxation times. After the initial radio frequency (rf) pulse (π/2), standard detection of the ^{29}Si free-induction decay occurs. After a time delay τ, application of a second rf pulse (π) refocuses the magnetization into a spin (Hahn) echo at a time 2τ. At the moment the echo occurs, a third rf pulse (π/2) forces the magnetization back to its equilibrium position along the longitudinal axis of the static magnetic field. After a short repetition delay, the process is repeated.

signal-to-noise. The DEFT experiment is shown schematically in Figure 3. After the initial $\pi/2$ rf pulse at time $t = 0$, standard detection of the ^{29}Si free-induction decay occurs. Normally thereafter, a delay of duration 5−10 times T_1 would be required for the net magnetization to reequilibrate along the *z*-axis of the static $\boldsymbol{B}_0$ magnetic field after the initial excitation pulse. In the DEFT experiment, however, a refocusing pulse at time $t = \tau$ (on the order of tens of ms) is applied instead, which results in formation of a spin (Hahn) echo at time $t = 2\tau$. Coincident with the echo, another $\pi/2$ pulse is applied to direct the ^{29}Si magnetization back to the *z*-axis, thus forcing the system back to "equilibrium" a few milliseconds after data acquisition has been completed (as opposed to the tens or hundreds of seconds required for the usual T_1 criterion). In this way, an order of magnitude or more increase in signal sensitivity can be achieved. Furthermore, separate proton or double resonance coils are not needed to facilitate magnetization transfer, as in methods that rely on scalar couplings.

RESULTS AND DISCUSSION

Figure 4 shows a solution-state DEFT ^{29}Si NMR spectrum of 800 μM (22.4 μg/mL) 96% ^{29}Si-enriched aqueous silicic acid (H_4SiO_4) at pH ≈ 8 acquired using the large-diameter coil and probehead shown in Figure 1. This concentration of dissolved silica is comparable to the concentration of soluble silicic acid in normal seawater. A repetition delay of 1 s was used, and 10 800 acquisitions were averaged over a period of 3 h. The $\pi/2$ pulse width used in this case was approximately 60 μs. Large pulse

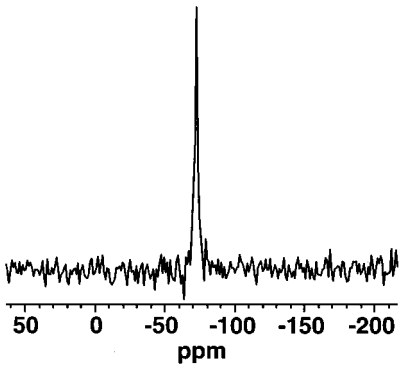

Figure 4. DEFT ^{29}Si NMR spectrum of 800 μM silicic acid (96% enriched in ^{29}Si) in Nanopure water at room temperature. A total of 10 800 signal averages were acquired using a repetition delay of 1 s (total measurement time of 3 h). The signal-to-noise ratio is 16 with a line width of approximately 31 Hz. The signal is referenced to tetramethylsilane (TMS).

widths are to be expected due to the large coil diameter, and this leads to several experimental complications, which are discussed below. The maximum transmitter power (<1 kW) that can be used without arcing difficulties depends on the ionic strength of the sample; higher power levels are possible with more concentrated solutions. In Figure 4, a single ^{29}Si peak is observed at −71 ppm with a line width of 31 Hz. Line widths of 30 to 60 Hz have been obtained for all silicate solution samples that we have studied to date using the large-coil probehead (sample volume = 27 cm^3). For comparison, solution-state ^{29}Si line widths were measured to be 5−10 Hz for aqueous silicic acid in ^{29}Si NMR spectra acquired on the same spectrometer with a 7-mm commercial probehead (sample volume = 0.6 cm^3) under otherwise identical conditions. In both cases, the line widths are attributed to inhomogeneities in the static $\boldsymbol{B}_0$ fields, which tend to become greater as the sample volume increases. The measured signal-to-noise (S/N) ratio is 16, which indicates a minimum detection limit (S/N = 2) of approximately 80 μM ^{29}Si-enriched silicic acid in 3 h. For comparison, an 800 μM silicic acid solution containing ^{29}Si in natural abundance (i.e., 37.6 μM ^{29}Si) would require an estimated measurement time of approximately 6 h to achieve a minimum S/N ratio of 2.

These results reflect significant sensitivity improvements for detecting dilute ^{29}Si species in aqueous solutions. For example, applying the DEFT experiment on the same ^{29}Si-enriched 800 μM silicic acid solution at 11.7 T (^{29}Si resonance frequency = 99 MHz) using a conventional commercial NMR probehead (7-mm diameter, 1.5-cm long, 0.6 cm^3 coil) yielded no detectable ^{29}Si signal after the same 3-h measurement time. Second, using the large coil alone (31-mm diameter, 4.7-cm-long, 35 cm^3 coil) without the DEFT technique (i.e., using a standard one-pulse sequence), it is estimated that approximately 2 weeks would be required to obtain a detectable (S/N = 2) ^{29}Si signal on the ^{29}Si-enriched 800 μM silicic acid solution. This is based on the one-pulse signal obtainable from pure natural abundance TMS and the difference in ^{29}S concentrations between the two samples (345 mM for TMS). Finally, this approach is not limited by the strengths of scalar couplings, which are not used or required to obtain the signal enhancements measured in the present study. Indeed, under the conditions employed here, the rapid exchange dynamics between the hydrogen atoms of silicic acid and those of water average such

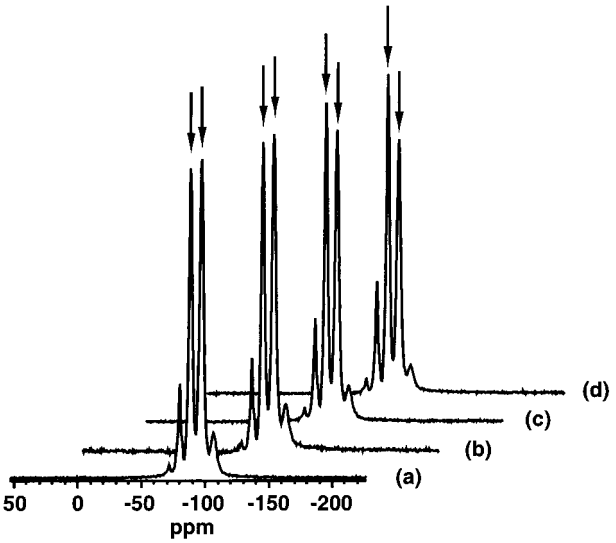

Figure 5. Solution-state ^{29}Si NMR spectra of 27 wt % SiO_2 in a 40 wt % NaOH solution. (a) A quantitative one-pulse spectrum obtained using a 60-s repetition delay. The remaining ^{29}Si spectra were acquired with the DEFT pulse sequence (Figure 3) using different repetition delays: (b) 4, (c) 2, and (d) 0.25 s.

couplings, thereby precluding the use of polarization transfer methods to obtain significant sensitivity improvements on dilute silicic acid.

While the use of the large-diameter NMR coil and DEFT technique provides substantial signal enhancements for dilute aqueous silicate species, the integrated peak areas may not reflect relative species concentrations. Because the range of excited frequencies in pulse NMR is inversely proportional to the duration of the rf pulse, a large pulse width will lead to difficulties in systems with large chemical-shift ranges. Peak intensities may be significantly different, depending on what part of the spectrum is excited on-resonance, as a consequence of the finite excitation range of the rf pulses. In addition, the DEFT sequence is not, in general, quantitative. The limitations of the DEFT technique, as well as the conditions that yield maximum signal enhancement, have previously been reported in the literature.[10,11] The signal amplitude in the DEFT experiment is a function of not only the longitudinal (T_1) and transverse (T_2) relaxation rates, which will generally be different for different species, but also of the repetition rate.[11] This is demonstrated in Figure 5, which compares a standard one-pulse solution-state ^{29}Si NMR spectrum (Figure 5a) acquired using a 60-s repetition delay to three DEFT ^{29}Si spectra (Figure 5b−d) acquired using different repetition delays for the same solution (27 wt % unenriched SiO_2 in 40 wt % aqueous NaOH) under otherwise identical conditions. The five ^{29}Si peaks observed are attributed to the following silicate species:[16,17] monomeric anions (−71 ppm), dimer and/or cyclic trimer anions (−81 ppm), cyclic quatrimer and/or double-three-ring (D3R) oligomeric anions (−89 ppm), double-four-ring (D4R) oligomeric anions (−99 ppm), and silicate anions in which ^{29}Si species experience 5-fold coordination with oxygen (−105 ppm). It is evident that the relative intensities of the two largest peaks change

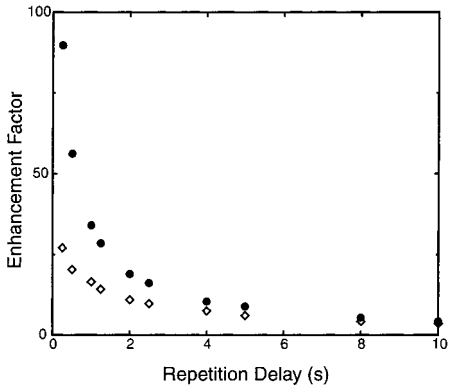

Figure 6. ^{29}Si NMR sensitivity enhancements produced using the large-diameter NMR coil and probehead (Figure 1), in conjunction with the DEFT experiment (Figure 3), for (◇) tetramethylsilane (TMS) and (●) double-four-ring (D4R) silicate anions in aqueous solution. The repetition delay was varied while the total experiment time was kept constant at 160 s for TMS and 640 s for the D4R silicate solution. Peak areas are normalized to the areas obtained using a 40-s repetition delay.

in Figures 5b−d as the repetition time changes. Thus, while it is possible to decrease the repetition delay and thereby increase the number of scans and S/N for a given measurement time, this may occur at the expense of signal quantitativeness. In this particular example, it is possible to obtain a DEFT ^{29}Si NMR spectrum (Figure 5b) that matches the quantitative one-pulse spectrum (Figure 5a) by using a relatively short repetition delay (4 s) in the DEFT experiment. By comparison, polarization transfer approaches are inherently nonquantitative, because of diverse scalar coupling strengths associated with species with different proton neighbors and/or different dynamic behaviors. The DEFT experiment is more likely to be able to detect quantitatively the different species present in multicomponent mixtures, including aqueous silicate solutions, whose components would not be easily detected using polarization transfer methods.

Figure 6 shows the variation in the ^{29}Si NMR signal intensity (peak area) with varying repetition delay (RD) for two liquid samples, TMS and an alkaline aqueous solution of double-four-ring (D4R) silicate anions, both with ^{29}Si in natural abundance and the total measurement times held constant. A substantial degree of signal enhancement and savings in experimental time can be achieved by using the DEFT experiment, in conjunction with the large-diameter NMR coil. For each sample, the repetition time was varied from 0.25 to 40.0 s and the number of scans was adjusted to keep the total time of each experiment fixed at 160 s for TMS or 640 s for the D4R silicate anion solution. A fixed τ value of ∼26 ms was used for both sets of measurements. Thus, for the same total measurement time, the experiments for RD = 0.25 s permit 160 times the number of signal acquisitions as those for RD = 40 s. Nearly 30- and 100-fold increases in ^{29}Si signal sensitivity result from the use of the DEFT pulse sequence for TMS and the D4R solution samples, respectively. The different signal enhancements observed are due to the different ^{29}Si relaxation behaviors of the two species: the measured T_1 relaxation times were 16.2 s for TMS and 5.3 s for the D4R species, with the corresponding T_2 relaxation times measured to be 0.28 and 1.0 s, respectively. The observed enhancements are consistent with those calculated using expressions derived by Carlotti et al.[11]

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CONCLUSIONS

A combination of NMR probehead improvements and new methodology applications permit the characterization of dilute ^{29}Si solution species in moderate magnetic fields at substantially lower concentrations than previously possible. A probehead has been developed with a large-diameter solenoid coil possessing a nonuniform winding pattern that provides improved rf field homogeneity for large-volume samples. Such a design allows solution-state ^{29}Si samples, with volumes that are an order of magnitude larger than standard solenoid coils, to be measured with acceptable spectral resolution. Use of the DEFT NMR experiment, furthermore, permits more rapid signal averaging in cases where long longitudinal relaxation times otherwise require long repetition delays in standard detection schemes. The combination makes it possible to detect 800 μM aqueous silicic acid (96% enriched in ^{29}Si) in 3 h in a magnetic field of 4.2 T with a signal-to-noise ratio of 16 and a line width of 31 Hz. While sensitivity enhancements are functions of the DEFT repetition delay and species' NMR relaxation properties, quantitative peak intensity measurements are still possible. This approach, furthermore, is amenable to the detection of silica species undergoing rapid ^{1}H exchange and complements strategies at higher magnetic fields and those relying on scalar or dipolar couplings. Studies of dilute ^{29}Si in biologically relevant aqueous systems using this technique are currently underway in our laboratory.

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