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STRONG GRADIENTS FOR SPATIALLY RESOLVED DIFFUSION MEASUREMENTS

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A new multilayer approach to gradient coil design, which allows the production of very strong gradient coils with reasonable resistance and consequent power dissipation, has been developed. Using this approach we have designed and built a strong z-gradient coil that will accommodate vertically mounted samples contained in 5-mm nuclear magnetic resonance tubes. The coil has an efficiency of 1.73 $Tm^{-1}A^{-1}$, an inductance of 49 μH, and a resistance of 1.8 Ω, with a homogeneous volume consisting of a central cylinder of 4.5-mm length and diameter. This coil has been used to monitor the diffusion of water in Nylon 6.6 at room temperature, during desorption. This system is difficult to monitor via nuclear magnetic resonance (NMR), because the diffusion coefficients are typically less than 10^{-13} m^2s^{-1}, while the T_2 relaxation time is less than 1 ms even when the sample is fully saturated. The resulting measurements show a strong concentration dependence of the T_2 relaxation time and self-diffusion coefficient of the absorbed water. The measured concentration profiles are consistent with a Fickian diffusion process with a concentration-dependent diffusion coefficient. The measured self-diffusion values are in reasonable agreement with those inferred from the variation of the concentration profiles as a function of time, using the one-dimensional Fickian diffusion equation.

Keywords: **Multilayer gradient coil; Self-diffusion; Nylon 6.6.**

INTRODUCTION

Very large magnetic field gradients are required in a variety of nuclear magnetic resonance (NMR) experiments. In NMR microscopy, large field gradients are needed to achieve fine resolution, particularly in the "diffusion limited" regime, where diffusion under the read gradient is the dominant broadening mechanism.[1] In pulsed-gradient spin-echo (PGSE) experiments, strong field gradients are necessary for the measurement of diffusion in low-mobility systems and also allow the investigation of motion occurring on short time scales.[2] The diffusion coefficients of fluids absorbed in polymers can be several orders of magnitude less than that of the bulk fluid,[3] and often can only be measured by indirectly monitoring the variation of fluid concentration with position and time. Strong gradients allow NMR measurement of the spatial variation of the fluid self-diffusion coefficient in such systems, thus allowing more direct monitoring of the processes controlling fluid ingress.

Very large magnetic field gradients occur naturally in the fringe fields of conventional high field superconducting magnets. For example, the maximum rate of change of field with position below a 400-MHz, 89-mm bore superconducting magnet is about 60 Tm^{-1}.[4] Such gradients in the stray field have been widely employed in stray-field imaging (STRAFI)[4] experiments and in diffusion measurements.[5] The use of these systems in gradient generation has the advantage of giving large gradients of high stability over reasonably large volumes, but has the disadvantage of only providing a fixed magnitude gradient that can not be switched off. The permanent presence of the gradient poses some significant restrictions on the range of pulse sequences that can be implemented. Magnetic field gradients of similar magnitude, which can be rapidly switched on and off, and varied in magnitude offer some advantages.

To date, most experiments employing very large, switched magnetic field gradients have been based on the

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use of quadrupolar gradient coils.[6] Quadrupole gradient coils are based on wires wound on the surface of a cylinder, whose axis is normal to the applied magnetic field. This coil geometry has certain disadvantages for sample mounting, since in vertical bore magnets the sample must be mounted horizontally. Orientation of the sample with respect to the gradient direction is also not as straightforward as it is when using a conventional gradient coil, in which the coil cylinder axis is parallel to the applied field.

We have recently developed a new multilayer approach to coil design[7] that allows the design of very strong gradient coils with conventional cylindrical geometry. Using this approach it has been possible to produce a z-gradient coil that accommodates samples contained in standard 5-mm NMR tubes, while generating a gradient of 52 Tm^{-1} at 30-A current.[7] This coil has been used to monitor the desorption of water from Nylon 6.6 at room temperature, a system in which the diffusion coefficient is concentration dependent and at most 4 orders of magnitude less than that of free water, while the transverse relaxation time is less than 1 ms even at the highest water concentration.

Gradient Coil Design and Construction

In designing a gradient coil there is always a trade-off between gradient coil efficiency (η), inductance (L), resistance (R), and the size of the region within which the field variation is linear with position. Increased efficiency usually leads to worse linearity, higher inductance that, in turn, implies longer gradient rise times, and higher resistance, resulting in greater power dissipation in the coil.[8] The scaling of the above parameters with coil size means that the highest coil performance can be achieved using small coils and that for such coils the resistance and the consequent power dissipation in the coil constitute the limiting factor in achieving high gradient strengths. The resistance is the dominant factor, because high efficiency demands a large number of turns in the coil, the accommodation of which inevitably leads to a small current-carrying cross section. In fact, for a conventional gradient coil, a doubling of the efficiency via a factor of 2 increase in the number of turns leads to an eightfold increase in the coil resistance. A factor of 2 resulting from the increase in wire length, and a factor of 4 resulting from the twofold reduction in wire diameter needed to fit in the greater number of wires. This unfavourable scaling can be considerably improved upon by adopting a multilayer design in which the wires are allowed to spread out in three dimensions. In this situation, a doubling of the coil efficiency can be achieved at the cost of only a fourfold increase in resistance, since the current-carrying cross section only has to be reduced by a factor of 2 to double the number of wires.[7]

By making a minor extension to the theory used to design standard, single-layer, cylindrical coils,[8] we have been able to implement a multilayer approach to coil design.[7] The main aim of this work was the production of a very strong, z-gradient coil that would accommodate samples contained in standard 5-mm NMR tubes, operate in a static magnetic field of 11.7 T, and at a current of up to 50 A. We consequently aimed for a gradient coil with an inner diameter of 8 mm, which provided a usable volume within which the gradient deviated from linearity by less than 5%, consisting of a 4.5-mm diameter cylinder of 4.5-mm length. The coil length and outer diameter were not significantly constrained, but we aimed for a resistance of less than 2 Ω. In the light of the above, we positioned the inner layer at a radius of 4.5 mm. The final 120-turn, four-layer coil design had an efficiency of 1.73 $Tm^{-1}A^{-1}$, a resistance of 1.8 Ω, and an inductance of 49 μH.

A short, saddle radiofrequency coil with a sensitive volume matched to the homogeneous region of the gradient coil was wound on a former with 6-mm outer diameter and 5-mm inner diameter. The coil's efficiency and the size of its homogeneous volume were confirmed via simple imaging experiments.[7]

Diffusion of Water in Nylon 6.6

Previous NMR studies of the diffusion of water in Nylon have been based on indirect monitoring of the variation of absorbed fluid concentration as a function of position and time.[3] Using the strong gradient coil we have been able to extend the scope of earlier studies by directly measuring the spatial variation of the self-diffusion coefficient of the absorbed fluid during desorption.

In the present study, machined Nylon 6.6 cylinders of 4.2-mm outer diameter and 3.1-mm length were immersed in distilled water at 70°C until fully saturated. For examination by NMR imaging, the cylinder was fixed inside a 5-mm NMR tube, forming a snug fit so that water could only leave the sample via its two flat faces. A sealed capillary tube of 700-μm inner diameter, containing a small amount of distilled water was also placed inside the NMR tube. This water provided a reference signal in the experiments. One-dimensional imaging was carried out at room temperature after varying times of desorption ranging from 3–118 h. Measurements of T_2 and water concentration were made from 64 point profiles, generated using a standard spin-echo sequence (repetition time (TR) = 5 s, bandwidth (BW) = 125 kHz, number of excitations (NEX) = 8). This sequence was applied with 11 different echo times, ranging from 1.2–2.6 ms. T_1 values were measured by varying TR. Thirty-two-point, diffusion-weighted profiles were produced using a stimulated-echo sequence (TR = 5 s, BW = 125 kHz, NEX = 512), incorporating gradient

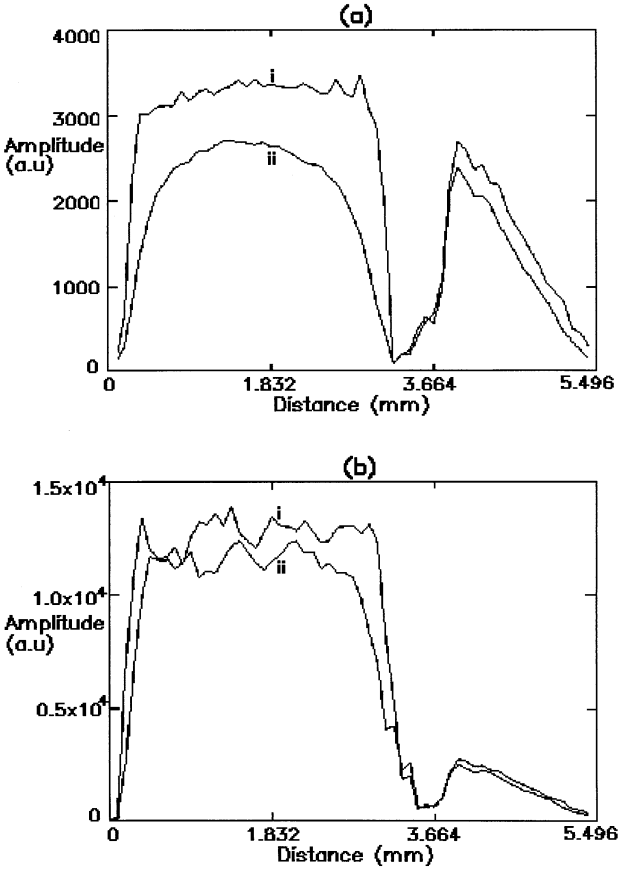

Fig. 1. (a) Profiles obtained using the spin echo sequence with 1.2-ms echo time after 3 (i) and 95 (ii) h of desorption. The resolution in these profiles is 91 μm. The small hump in the signal at the right side of the Nylon results from the water in the small capillary tube. (b) Concentration profiles obtained after 3 (i) and 95 (ii) h of desorption from exponentially fitting the signal variation in 11 T_2-weighted profiles.

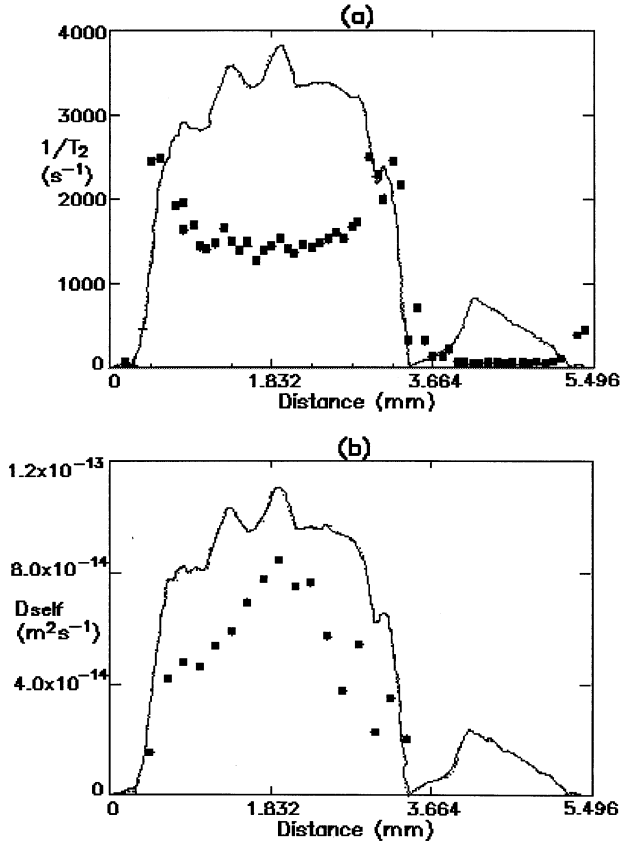

Fig. 2. (a) Spatial variation of $1/T_2$ (+) and water concentration (broken line) after 118 h of desorption. (b) Spatial variation of self-diffusion coefficient (+) and water concentration (broken line) after 118 h of desorption.

pulses of 432-μs duration, which were separated by 700 ms. The effective echo time in these experiments was 1.6 ms. Calculation of the spatial variation of the self-diffusion coefficient was based upon the use of nine such profiles with b-values ranging from 16.1–0.04 s μm^{-2}. The maximum gradient strength used was 41.5 Tm^{-1}. The spatial resolutions of the spin-echo and stimulated-echo data were 91 and 182 μm, respectively.

Figure 1a shows spin-echo profiles obtained at the shortest echo time for one sample after 3 and 95 h of desorption. The uniform saturation of the sample at the earlier time, and the reduction in signal at the edges of the sample at the later time as a result of water desorption are clear from these data. Figure 1b shows the concentration profiles obtained at the same times using the full set of T_2-weighted profiles. These show that much of the change in profile intensity with position, results from the effect of the T_2 variation with concentration. As a result of the T_2 weighting of the spin-echo sequence, this amplifies the reduction in signal occurring for a small decrease in concentration. A reduced concentration at the sample edges is still evident, however, in the concentration profile taken at the later time. Figure 2a shows the measured variation of concentration and $1/T_2$ in the same sample after 118 h of desorption (the latest time at which measurements were made). This figure more clearly shows that T_2 is highly concentration dependent, decreasing at lower concentrations where the water is less mobile, as found in earlier experiments.[3] The measured T_2 is always less than 1 ms even at the highest concentration. The measured T_1 relaxation time was consistently about 1.6 s, showing little variation with concentration. Figure 2b shows the diffusion profile obtained after 118 h of desorption. The measured diffusion coefficient is 4–5 orders of magnitude less than that of free water and shows a strong dependence on concentration.

Over the temperature range 20–100°C, the diffusion of water in Nylon has been reported to be Fickian, with a concentration-dependent diffusion coefficient.[3,9] The

diffusion of water may therefore be described by the one-dimensional form of Fick's diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right), \tag{1}$$

where C is the fluid concentration that is a function of both position (x) and time (t), and D is the concentration-dependent, transport diffusion coefficient.[10] For times up to 120 h, the process of water desorption from one face of the Nylon block can be approximated as that occurring in a semi-infinite system with boundary conditions, $C = 0$ for $x > 0$ at $t = 0$ and $C = C_0$ at $x = 0$ for $t \geq 0$ (C_0 is the concentration of water in saturated Nylon). Under these conditions the method of Matano[11] can be used to measure the variation in the diffusion coefficient with concentration. To apply this method to our data, the concentration profiles measured at eight different times were collapsed onto a single master plot of C/C_0 vs. $x/t^{1/2}$. The slope and integral of the resulting best-fitting curve are then used to calculate D as a function of C/C_0. The resulting data are shown in Fig. 3a. The large error bars mainly result from significant errors in the calculation of the slope. Figure 3b shows the directly measured values of the self-diffusion coefficient in the same sample, plotted as a function of the scaled concentration. These data are taken from diffusion measurements made at eight different desorption times. Comparison of Fig. 3, a and b, indicates a broad agreement between the diffusion coefficients measured by the two different methods, with both showing maximum values of approximately 10^{-13} m^2s^{-1} and a reduction with decreasing concentration. The Matano method does, however, yield a significantly larger diffusion coefficient at the lower concentrations, which is currently unexplained.

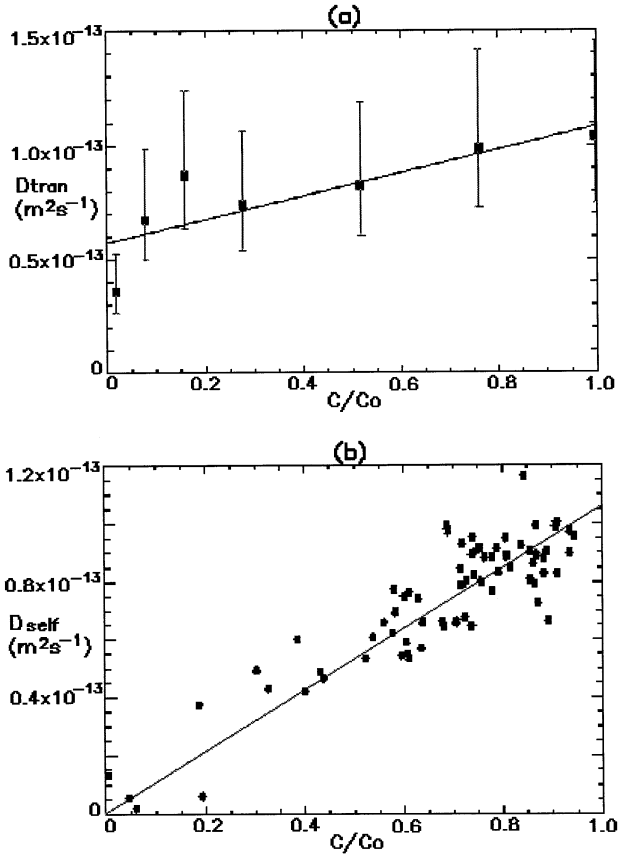

Fig. 3. (a) Variation of the diffusion coefficient measured from the condensed plot of C/C_0 vs. $x/t^{1/2}$ using the method of Matano as a function of scaled concentration. This data were generated from profiles measured at eight different times of desorption. (b) Variation of the self-diffusion coefficient, measured using the STE sequence, as a function of scaled concentration. The data are taken from diffusion profiles measured at eight different times of desorption.

CONCLUSION

Using a new multilayer approach to coil design we have been able to design and construct a strong gradient coil system that will accommodate vertically mounted samples contained in 5-mm NMR tubes. The coil generates a gradient of 52 Tm^{-1} at a current of 30 Å and has a reasonably low inductance of 49 μH and a resistance of 1.8 Ω, leading to acceptable amplifier driving voltage requirements (e.g., 54 V at 30 Å), and tolerable power dissipation for many sequences. Water cooling of the coil will be required if significant duty cycles at the highest currents are needed.

This coil has been used to monitor the diffusion of water in Nylon 6.6 at room temperature, during desorption. This system is difficult to monitor via NMR, because the diffusion coefficients are typically less than 10^{-13} m^2s^{-1}, while the T_2 relaxation time is less than 1 ms even when the sample is fully saturated. The resulting measurements show a strong concentration dependence of the T_2 relaxation time and self-diffusion coefficient of the absorbed water. The measured concentration profiles are consistent with a Fickian diffusion process with a concentration-dependent diffusion coefficient, as seen previously.[3] Using the method of Matano, transport diffusion values have also been calculated from the measured concentration profiles. The resulting values are in reasonable agreement with the self-diffusion coefficients measured directly. This work confirms the feasibility of using large, switched magnetic field gradients to make diffusion measurements in very low mobility systems. Future work will be directed toward non-Fickian systems where indirect measurement of diffusion coefficients is not possible.

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