Self-diffusion measurements by a mobile single-sided NMR sensor with improved magnetic field gradient

D.G. Rata, F. Casanova, J. Perlo, D.E. Demco, B. Blümich *

Institut für Technische Chemie und Makromolekulare Chemie, Rheinisch-Westfälische Technische Hochschule, Worringerweg 1, D-52056 Aachen, Germany

Abstract

A simple and fast method of measuring self-diffusion coefficients of protonated systems with a mobile single-sided NMR sensor is discussed. The NMR sensor uses a magnet geometry that generates a highly flat sensitive volume where a strong and highly uniform static magnetic field gradient is defined. Self-diffusion coefficients were measured by Hahn- and stimulated echoes detected in the presence of the uniform magnetic field gradient of the static field. To improve the sensitivity of these experiments, a Carr–Purcell–Meiboom–Gill pulse sequence was applied after the main diffusion-encoding period. By adding the echo train the experimental time was strongly shortened, allowing the measurement of complete diffusion curves in less than 1 min. This method has been tested by measuring the self-diffusion coefficients D of various organic solvents and poly(dimethylsiloxane) samples with different molar masses. Diffusion coefficients were also measured for n-hexane absorbed at saturation in natural rubber with different cross-link densities. The results show a dependence on the concentration that is in good agreement with the theoretical prediction. Moreover, the stimulated-echo sequence was successfully used to measure the diffusion coefficient as a function of the evolution time in systems with restricted diffusion. This type of experiment proves the pore geometry and gives access to the surface-to-volume ratio. It was applied to measure the diffusion of water in sandstones and sheep Achilles tendon. Thanks to the strong static gradient G_0, all diffusion coefficients could be measured without having to account for relaxation during the pulse sequence.
© 2006 Elsevier Inc. All rights reserved.

Keywords: NMR; Self-diffusion; Static gradient; Unilateral NMR; Cross-linked elastomers; Porous media; Achilles tendon; Restricted diffusion

1. Introduction

In the last years, several applications of NMR in strongly inhomogeneous magnetic fields have been developed. Large field gradients are desired in experiments like STRAFI to image hard materials with high spatial resolution [1], but they are pointed out as disadvantageous in single-sided NMR, where off-resonance effects across the sample complicate the performance of conventional pulse sequences, and reduce the sensitivity during the detection [2,3]. Consequently, the use of open NMR sensors for non-destructive sample characterization required reexamination of conventional pulse sequences to measure relaxation times [4–6], multiple quantum coherences [7,8], images [9,10], and mass transport [11,12], eliminating distortions due to the presence of unavoidable field inhomogeneities. This type of sensor has been successfully applied in material testing [13,14], biomedicine [15], and well logging [16]. Moreover, the first steps toward high-resolution NMR spectroscopy in inhomogeneous fields have been taken and the first ex situ spectra have recently been measured [17–20].

Although in the cases mentioned above, the presence of the static gradient represents a complication to extract the desired information, some applications like high-resolution sample profiling or measurements of diffusion coefficients benefit from it. The biggest difficulty that is faced with an open magnet is the generation of a uniform gradient. Recently, we have presented a simple magnet geometry

---
* Corresponding author. Fax: +49 241 80 22 185.
   E-mail address: bluemich@mc.rwth-aachen.de (B. Blümich).

that produces a strong and highly uniform gradient at a defined distance from the magnet surface [21]. It has been used to measure sample profiles with a spatial resolution better than 5 μm, a technique that has opened important new applications to NMR that range from in vivo skin measurements to the characterization of objects of cultural heritage [21,22]. In this paper, we exploit the strong and uniform static gradient of this magnet to measure self-diffusion in a variety of materials to reveal the sample microstructure.

In many systems molecular self-diffusion provides important information on molecular organization and interactions of mobile molecules with the environment. The effect of molecular self-diffusion on the amplitudes of the Hahn and the stimulated echoes in a strong static magnetic-field gradient has been analyzed theoretically and experimentally in recent years [23–29]. The use of strong static gradients such as the one found in the stray field of superconducting magnets, allows measurements of root-mean square molecular displacements as small as 20 nm and self-diffusion coefficients as small as 10^{-16} m^2/s. Large gradients simplify measurements of the diffusion coefficient in heterogeneous materials like porous materials and biological systems, since it reduces the relative contribution from background gradients due to susceptibility variation across the sample. This is so because the background gradients are proportional to the magnitude of the applied static field B_0 but essentially independent of the field gradient. From this point of view, measurements with unilateral low field NMR sensors, which produce relatively strong field gradients, offer an interesting advantage over conventional methods.

Although the possibility of using the strong gradient of an open magnet to measure diffusion has been mentioned in the very first papers about inside-out NMR [2], the need of a uniform gradient complicated the use of hand-held unilateral NMR sensors for accurate determination of diffusion coefficients. The problem was recently alleviated with the implementation of a numerical procedure that deconvolutes the spatial variation of the static field gradient [30]. However, the method requires knowledge of the spatial distribution of both, the B_0 and B_1 fields, and the assumption of a uniform diffusion coefficient D across the sample. It was applied to measurements done with a bar magnet NMR-MOUSE®, where D was extracted for a series of liquids with different viscosities. The effect of relaxation in these self-diffusion measurements was overcome by means of a constant-relaxation method [23,25,30]. The simple pulse sequence $\theta_x - \tau_1 - 2\theta_y - \tau_1 + \tau_2 - 2\theta_y - \tau_2 - Hahn\ echo$ was used to determine the self-diffusion coefficient D at constant-relaxation condition, i.e., for $\tau_1 + \tau_2 = const$ in the presence of strongly inhomogeneous static and radio-frequency magnetic fields [30]. The method was shown to be particularly useful for measuring D of solvents in elastomers without the need to measure the transverse relaxation rates. Although this numerical procedure provides an alternative to measure diffusion even in the presence of non-uniform

gradients, it suffers from limited accuracy compared to conventional techniques like STRAFI. The most important drawback is the need of the B_0 map to extract the distribution of static gradient, a calculation that is an important source of errors.

In this paper, we take advantage of a simple magnet geometry that generates a highly uniform and strong gradient [21] to measure the self-diffusion coefficient of protonated molecules with high accuracy and in very short experimental times. The effect of self-diffusion was encoded in the amplitudes of the stimulated and Hahn echoes generated in the presence of the static magnetic field gradient. The sensitivity of these experiments was improved by applying a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence after the diffusion-encoding period. Both sequences have been tested by measuring D of various organic solvents, and poly(dimethylsiloxane) (PDMS) samples with different molar masses. The Hahn-echo sequence was used to measure D for n-hexane absorbed at saturation in a natural rubber samples with different cross-link densities. Moreover, the stimulated-echo sequence was used to measure the dependence of the diffusivity on the diffusion time in a water-saturated sandstone as well as in Achilles sheep tendon.

2. Experimental

2.1. Single-sided NMR sensor

The unilateral NMR sensor, used in this work takes advantages of a magnet specially designed to generate a magnetic field with a uniform gradient in the sensitive volume [21]. The geometrical configuration of the permanent magnet is shown in Fig. 1 [21]. It consists of four permanent magnet blocks positioned on an iron yoke. The direction of polarization of each magnet block is indicated by the shades of gray. Magnets with the same polarization are separated by a small gap d_S while magnets with oppo-
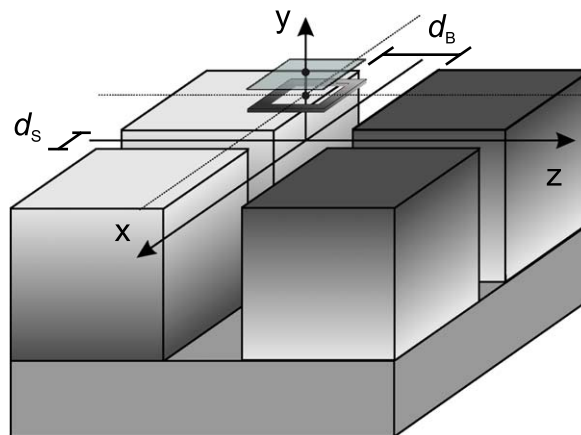

Fig. 1. The magnet geometry used for the one-sided NMR sensor with improved magnetic field gradient uniformity [21]. It consists of four permanent magnet blocks positioned on an iron yoke. The direction of polarization of the magnets is indicated by the gray shades.