

COMMUNICATIONS

Self-Diffusion Measurements by Carbon-13 NMR Using Radiofrequency Field Gradients

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This paper demonstrates the feasibility of self-diffusion measurements by radiofrequency field gradients with equipment tuned to the carbon-13 resonance frequency (i.e., 50 MHz for a field of 4.7 T). For the first time, self-diffusion coefficients of carbon disulfide and carbon tetrachloride are measured by NMR. The agreement with results from tracer methods is excellent. © 1998 Academic Press

Self-diffusion measurements by the conventional pulsed field gradient (PFG) spin echo method (1) based on ¹³C observations are rather scarce (2, 3); actually, they have been employed in rare instances when carbon-13 was the only possible probe for attaining such information. Two problems are indeed encountered with carbon-13 PFG experiments. First, the low natural abundance may entail sensitivity limitations; as a matter of fact, the recourse to enriched materials was systematic: 30% enrichment for the C₆₀ fullerene (2) and 90 and 50% enrichment for, respectively, CO and CO₂ in zeolites (3). The other problem concerns the efficiency of the gradient which, in practice, is lowered by a factor of 4 (with respect to proton measurements), because it acts through the expression γg , where g is the gradient amplitude (independent of the observed nuclei in the case of static field gradients) and γ the gyromagnetic ratio.

In the course of the setup of a probe devised for one-dimensional imaging by a radiofrequency field gradient (B_1 gradient) under CP/MAS conditions, we carried out a series of diffusion measurements *on liquid samples* with the objective of assessing the gradient quality and efficiency. As shown in Fig. 1, the probe has been constructed from an early Bruker arrangement from which we retained the probe body and the spinning assembly (for Andrew-type rotors).

It was decided that the B_1 gradient would be generated by a coil whose axis coincides with the spinning axis, and whose location is appropriate in order to make sure that the gradient is uniform over the whole sample (4, 5). As a first consequence of this choice, one must define an appropriate geometry for the doubly tuned (¹H, ¹³C) coil employed for the purely spectroscopic operations (excitation and detection). This is because the leakage with the gradient coil must be minimal (ideally zero), implying that the two coils must be electrically orthogonal. The solenoid usually implemented in CP/MAS probes cannot obviously fulfill this condition so that we turned to a saddle coil whose characteristics should permit decoupling and cross-polarization along with a quality factor high enough for reasonable ¹³C sensitivity. These features will be described in more detail elsewhere; for the moment, one can quote a 7- μ s 90° pulse for ¹³C and ¹H output power of about 1000 and 100 W, respectively. The residual leakage between the two coils can be further minimized by optimizing their relative orientation. In practice this is accomplished by gently rotating the saddle coil around its axis; this mechanical tuning leads typically to a residual leakage as low as 1%.

Once all instrumental problems have been solved, one still must face the sensitivity issue which is somewhat acute, as it was determined by trial and error that the zone where the gradient is uniform corresponds to a 4-mm-i.d. cylinder of 4-mm height (by uniform we mean a gradient having the same magnitude and direction over the whole sample; this property is presumably more essential in imaging experiments than in diffusion experiments). This evidently represents a tiny volume and any improvement in sensitivity would be welcome. The first liquid sample investigated was benzene and nuclear Overhauser enhancement was considered. Unfortunately, although composite pulse decoupling (Waltz-16) requiring a modest power and therefore producing little heat dissipation was used, we arrived at diffusion

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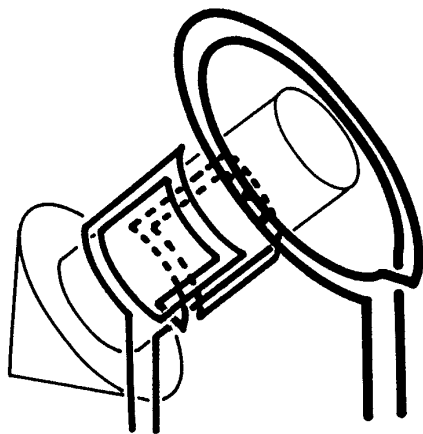


FIG. 1. Schematic view of the coil system adapted to CP/MAS conditions (Andrew-type rotor). The two-turn coil at the top generates the B_1 gradient. The saddle coil (also made of two turns) is doubly tuned for proton (200 MHz) and carbon-13 (50 MHz) and serves for the usual spectroscopic operations (excitation, decoupling, cross-polarization, detection). The two coils are assumed to be orthogonal.

coefficients whose values appear to be erroneous. This can presumably be ascribed to convection effects as already mentioned in the literature (6). We therefore decided to proceed by gating on decoupling only during acquisition periods. On the other hand, still for sensitivity reasons, reducing relaxation delays between consecutive measurements turned out to be mandatory. For that purpose, a very small quantity (1% in weight) of a relaxation reagent, iron(III)acetylacetonate, was systematically added to all substances investigated. As evidenced by the results obtained, this relaxation reagent did not affect the translational properties of the molecules considered and enables one to reduce the repetition rate down to 5 s (for all substances investigated here), thus making the accumulation process more efficient. The sample was rigidly fixed and its temperature was set in all cases to 25°C by a strong flow of preconditioned air. The temperature was measured and checked before and after each measurement by a thermocouple located close to the sample. Moreover, even when this was not necessary (for CCl_4 and CS_2 , see below), proton decoupling was gated on during the acquisition interval so that strictly identical conditions prevail for all samples and make meaningful comparisons possible.

Diffusion measurements were carried out with the simple sequence (7, 8)

$$(\delta g_1)_x - \Delta - (\delta g_1)_{\pm x} - (\pi/2) - \text{Acq.}$$

Here $(\delta g_1)_x$ stands for a B_1 gradient pulse of duration δ applied along the x axis of the rotating frame; Δ is the so-called diffusion interval and has been set to 200 ms for all experiments reported in this paper; and $(\pi/2)$ is a homoge-

neous read pulse. The elementary phase cycle $(\delta g_1)_{\pm x}$ ensures that only signals stemming from longitudinal magnetization, possibly affected by translational motion processes, are accumulated. The diffusion coefficient D is deduced from the evolution of the NMR signal as a function of δ proportional to $\exp(-\gamma^2 g_1^2 \delta^2 D \Delta)$. This sequence applied to benzene (carbon-13 in natural abundance) whose self-diffusion is precisely known at 25°C ($D = 2.21 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) yields a gradient amplitude of 21.2 $\text{G} \cdot \text{cm}^{-1}$ obtained for an amplifier output of about 300 W. All experiments reported in this work have been performed with a homemade spectrometer (9) built around a 4.7-T wide-bore magnet and a Bruker B-LAX 300 amplifier was used for RF supply to the gradient coil.

At this point, a comment can be made about B_1 gradients whose amplitude actually depends on the measurement frequency. By contrast with B_0 gradients whose amplitude is evidently the same regardless of the observed nucleus, B_1 gradients can be increased to compensate for the gyromagnetic ratio (e.g., at the ^{13}C resonance frequency with regard to the ^1H frequency). This is due to the fact that the RF gradient is proportional to B_1 at the center of the coil; the latter can be enhanced at lower frequencies simply by improving the coil quality factor (for instance, by adding one more turn to the coil and thus increasing its self-inductance). Therefore, as far as diffusion measurements are concerned (or imaging experiments), what is lost by the gyromagnetic ratio can be largely regained by the increase of the coil quality factor. A further check of the ability to measure self-diffusion coefficients by ^{13}C at the natural abundance level using B_1 gradients was provided by cyclohexane. (Both cyclohexane and benzene were chosen as first examples be-

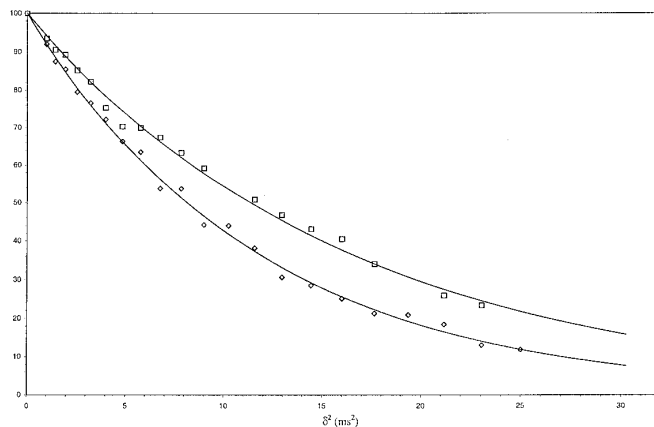


FIG. 2. Experimental data points corresponding to self-diffusion measurements by B_1 gradients through ^{13}C NMR. One hundred twenty-eight transients were accumulated for each point in the case of benzene (\diamond) and 200 in the case of cyclohexane (\square). Other experimental details are given in the text. Continuous curves have been recalculated from parameters fitted to the experimental data.

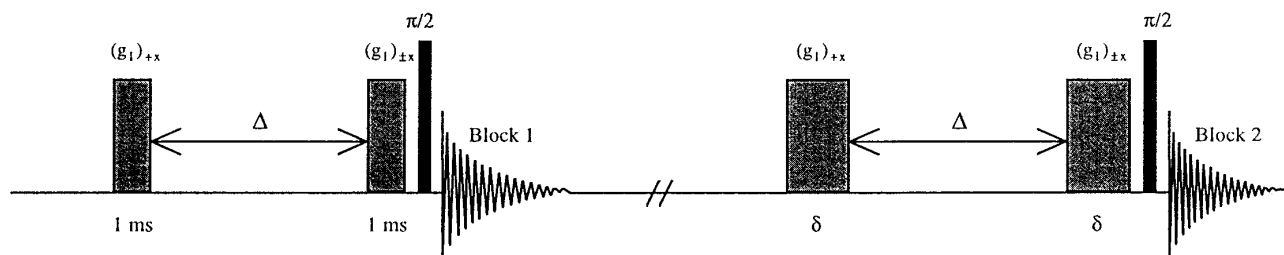


FIG. 3. The pulse sequence used for measuring self-diffusion coefficients by B_1 gradients through ^{13}C NMR when long-term averaging is necessary (gray rectangles correspond to B_1 gradient pulses whereas black bars correspond to normal "homogeneous" RF pulses). In order to compensate for any experimental drift, the actual data point (corresponding to a gradient pulse of duration δ) is possibly rescaled to a reference experiment (gradient pulse length of 1 ms). This is made possible and meaningful by alternate accumulation in two separate memory blocks.

cause of their high intrinsic sensitivity due to their six equivalent carbons per molecule.) Taking the gradient value derived from the benzene experiment, we find a self-diffusion coefficient of $1.51 \pm 0.03 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in perfect agreement with the value quoted in the literature (10). The experimental decays for both benzene and cyclohexane, along with the recalculated curves resulting from an appropriate fit, are shown in Fig. 2. Errors indicated throughout have been deduced from the comparison of two results: one obtained from a fit with the actual data, and the other with data randomly perturbed according to an estimate of the experimental uncertainty.

We turn now to a much more difficult problem which is the determination by NMR of the self-diffusion coefficient of carbon tetrachloride and carbon disulfide. The best nu-

cleus for such a determination is evidently carbon-13 and we decided to rely on nonenriched material. Although this may appear as an unnecessary challenge, it is certainly interesting to test the present method (by B_1 gradients) in extreme conditions. Due to very weak sensitivity, a large number of transients must be accumulated (as many as 16,000 for the largest δ values). Consequently, we decided to interleave reference and actual measurements as shown in Fig. 3. In this way, reliable data could be obtained, of course at the expense of extensive measuring times (see Fig. 4). It can be mentioned that self-diffusion coefficients of CCl_4 and CS_2 have not been previously measured by NMR (to the best of our knowledge). The average literature values (obtained by the radioactive tracer method or by light scattering) are $D = 1.34 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for CCl_4 (11) and $D = 4.21 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for CS_2 (12). From the data of Fig. 4, we find respectively $D_{\text{CCl}_4} = 1.34 \pm 0.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{CS}_2} = 4.39 \pm 0.02 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

These latter results demonstrate the consistency of the approach developed in this paper and, in particular, establish the capabilities of the B_1 gradient method for determining self-diffusion coefficients by carbon-13 NMR, at the natural abundance level.

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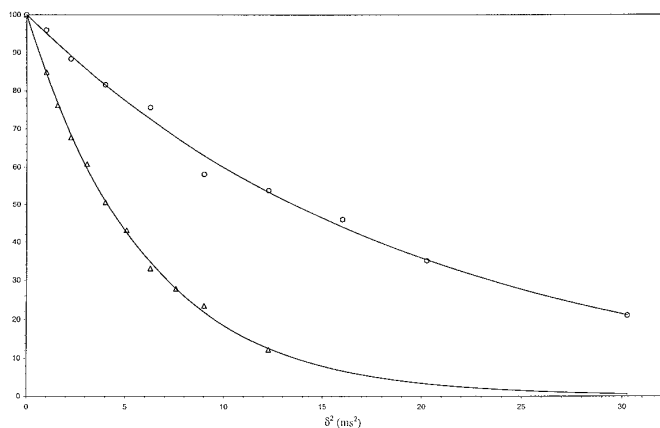


FIG. 4. Experimental data points leading to the self-diffusion coefficients of carbon disulfide and carbon tetrachloride. The sequence of Fig. 3 was used; experimental parameters were not given in the figures: Δ , CS_2 ; \circ , CCl_4 ; $\Delta = 200 \text{ ms}$; recycle time, 5 s; number of scans: CCl_4 , 8400 except for the last δ value (16,000); CS_2 , 7600 except for the last δ value (16,000). Continuous curves have been recalculated from parameters fitted to the experimental data.

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