

DIRECT MEASUREMENT OF DIFFUSION IN LIQUID PHASE BY ELECTRON SPIN RESONANCE

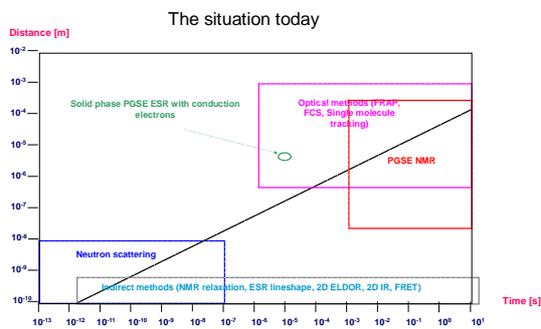
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Abstract

The critical roll of diffusion in the mechanism of various biological and chemical processes has led researches to an ongoing search for methods to measure diffusion coefficient. The measurement of diffusion over relatively long distances (during a period of milliseconds) can be carried out with techniques such as nuclear magnetic resonance (NMR) or fluorescence recovery after photo-bleaching (FRAP), and are quite established. However, methods for the direct measurements of diffusion over short distances (1-250 nm) during a period of ~ microseconds, have not yet been developed. Here we show that by utilizing a well known NMR pulse sequence (pulse gradient spin echo - PGSE), in an electron spin resonance (ESR) experiment, one can measure such short range diffusion. In order to adapt PGSE to ESR we had to develop high sensitivity micro-resonators and a capability to generate very intense and short gradient pulses of ~1 microsecond in length and ~100 T/m in magnitude. Our preliminary work included the measurements of the diffusion coefficient of three types of radical solutions: trityl radical in water, N@C₆₀ in chloronaphthalene and N@C₆₀ in CS₂. The experimental results were compared to the theoretical diffusion coefficient calculated by the Stokes-Einstein equation, and revealed an excellent agreement. Restricted diffusion of trityl in water in porous media was also measured by ESR PGSE and showed good agreement with the theory.

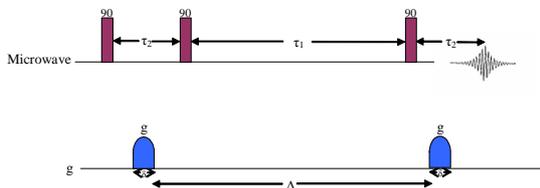
Motivation

Increase the time and distance ranges for measurements of diffusion and motion:



PGSE pulse sequence

The simulated echo pulse gradient is consisted of three 90° pulses and two gradient pulses as presented in the figure below.



The signal intensity is given by the following equation:

$$E = E_{t=0} \exp(-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3) - R)$$

$$R = \frac{2\tau_2}{T_2} + \frac{\tau_1}{T_1}$$

Where g is the intensity of the applied gradient pulse, D is the diffusion coefficient, γ is the gyromagnetic ratio, δ is the time duration of the gradient pulse, Δ is the time between the two gradient pulses. R is a constant that takes into account the relaxation process.

Signal equation for restricted diffusion in porous media of diameter $b/3$:

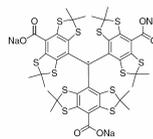
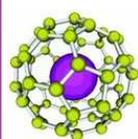
$$E_{\Delta}(q) = E_{\infty}(q) \cdot \exp\left(-\frac{6D_{eff}\Delta}{b^2 + 3\xi^2} \cdot \left(1 - \exp(-2\pi^2 q^2 \xi^2) \frac{\sin(2\pi qb)}{2\pi qb}\right)\right)$$

and ξ is the standard deviation of the pores size.

$$q = \gamma \cdot g \cdot \delta \cdot (2\pi)^{-1}$$

Experimental details

Three types of samples were tested:
N@C₆₀ in chloronaphthalene
N@C₆₀ in CS₂ and trityl in water.



A special tiny resonator was built for this system. It is composed of two Strontium Titanate (SrTiO₃) rings (O.D 1.4 mm, I.D 0.76 mm and height 0.9 mm).



Results

Unrestricted diffusion

The two plots represent the \ln magnitude of the stimulated echo signal as a function of $\bar{q} = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ for N@C₆₀ in chloronaphthalene (light blue) and in CS₂ (magenta), and for trityl in water (red). In plot (a) \bar{q} was varied by changing τ_1 in the pulse sequence and a simple normalization was applied. In plot (b), \bar{q} values were varied by changing the intensity of the gradient pulses, and the data of N@C₆₀ in chloronaphthalene was used as a reference to normalize the data for N@C₆₀ in CS₂.

Theoretical D values were calculated from the Stokes-Einstein equation, and were placed in the signal intensity equation in order to construct the theoretical graphs.

The Stokes-Einstein equation:

$$D = \frac{K_B T}{6\pi\eta r}$$

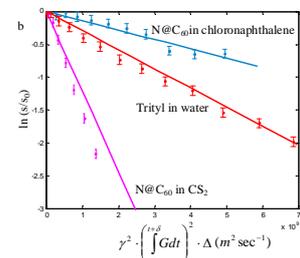
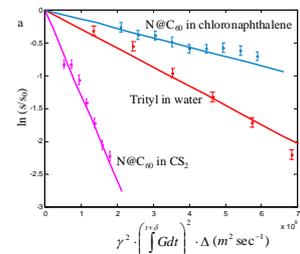
η Solvent viscosity

K_B Boltzmann constant

T Temperature

r Molecular radius

	Theoretical D	Empirical D experiment a	Empirical D experiment b
N@C ₆₀ in chloronaphthalene	1.4 · 10 ⁻¹⁰	1.0 · 10 ⁻¹⁰	1.5 · 10 ⁻¹⁰
N@C ₆₀ in CS ₂	1.2 · 10 ⁻⁹	1.2 · 10 ⁻⁹	1.6 · 10 ⁻⁹
Trityl in water	3.0 · 10 ⁻¹⁰	2.9 · 10 ⁻¹⁰	2.9 · 10 ⁻¹⁰

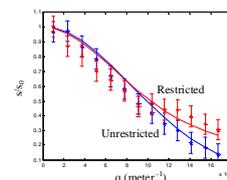


Results

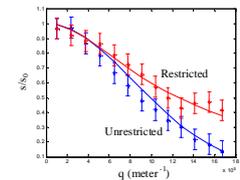
Restricted diffusion

Gradient was varied from 0 Tesla/meter to 100 Tesla/meter while all other parameters were kept constant.

Trityl motion in water in pores of 0.11 μm diameter and $\Delta=60$ μsec



Trityl motion in water in pores of 0.17 μm diameter and $\Delta=60$ μsec



Improved range of measurements

