

Ion pairing using PGSE diffusion methods

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1. Introduction

There is a continuing, indeed growing, interest in measuring diffusion constants and the literature reveals that a number of methodologies are in use. These include attenuated total reflection infrared spectroscopy (ATRIR) [1], capacity intermittent titration techniques (CITT) [2], long

capillary methods [3], and, of course, NMR spectroscopy, and these represent only a few of the various methods in current usage.

The use of pulsed field gradient NMR methods to measure diffusion constants dates back more than 40 years [4] and has been reviewed periodically [5,6]. In the pulsed field gradient spin–echo (PGSE) Stejskal–Tanner experiment, Fig. 1a, transverse magnetization is generated by the initial $\pi/2$ pulse which, in the absence of field gradients, dephases due to chemical shift, hetero- and homo-nuclear coupling evolution, and spin–spin (T_2) relaxation. After application of an intermediate π pulse, the magnetization refocuses, generating an echo.

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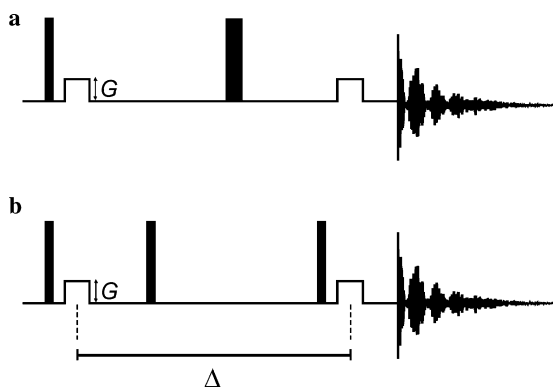


Fig. 1. Typical pulse sequences for the PGSE experiments: (a) the Stejskal–Tanner experiment; (b) the Stejskal–Tanner experiment, modified via substitution of two 90° pulses for a single 180° pulse. The Δ represents the time between the gradient pulses.

The first pulsed linear field gradient results in strong dephasing of the magnetization with a phase angle proportional to the length (δ) and the amplitude (G) of the gradient. Because the strength of the gradient varies linearly along, e.g., the z -axis, only spins contained within a narrow slice of the sample acquire the same phase angle. The second gradient pulse reverses the respective phases and the echo forms in the usual way. Of course the spins, which move out of their slice into neighbouring areas via Brownian motion, will not be refocused by the second gradient and this leads to an *attenuation* of the echo amplitude. As smaller molecules move faster, they translate during the time interval Δ into slices further apart from their origin, thus giving rise to smaller echo intensities for a given product of length and strength of the gradient.

The original relatively simple spin–echo sequence has since been replaced by a number of increasingly complicated pulse sequences and related data processing methods [7–12]. In the simplest improvement, the stimulated echo experiment, shown in Fig. 1b, the phase angles, which register the position of the spins, are stored along the z -axis in the rotating frame of reference by the action of the second $\pi/2$ pulse. The third $\pi/2$ pulse restores the transverse magnetization and the respective signal phases. This method is advantageous in that, during time Δ , T_1 , as opposed to T_2 , is the effective relaxation path during time Δ . Since T_1 is often longer than T_2 , the signal/noise ratio obtained is more favourable.

The diffusion part of the echo-amplitude can be expressed by as:

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2 G^2 \left(\Delta - \frac{\delta}{3}\right) D \quad (1)$$

where G is the gradient strength, Δ is the delay between the midpoints of the gradients, D is the diffusion coefficient, and δ is the gradient length. The diffusion coefficient, D , which is proportional to the slope of the regression line, is obtained by plotting $\ln(I/I_0)$ (I/I_0 = observed spin–echo intensity/intensity without gradients) vs. either Δ , δ^2 , $(\Delta - \delta/3)$ or G^2 .

2. Diffusion and the Stokes–Einstein relation

The experimental values for diffusion constants are usually given in units of $10^{-10} \text{ m}^2 \text{ s}^{-1}$ and this unit will be used in the discussion and the tables which follow. Naturally, these values are not as familiar to chemists as NMR chemical shifts, so that it is routine to report both the D -value and the hydrodynamic radius, r_H , of the molecule *via* the use of the Stokes–Einstein relation.

$$D = \frac{kT}{6\pi\eta r_H} \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, η the viscosity and r_H the hydrodynamic radius.

This equation assumes a spherical shape for the molecules in question (rarely correct). However, this relation does allow a correction for the different solution viscosities associated with the various solvents commonly in use. Indeed, it is possible to calculate an unknown viscosity for a solution at fairly low temperature by using a measured D -value on a reference substance and we shall return to this point.

Gierer and Wirtz [13] have derived a modified expression for the denominator of Eq. (2), which introduces the so-called friction coefficient, f , of a solute in a solvent. The solvent molecules are considered as spheres with radius r_{solvent} and not as a continuous medium.

$$f = \frac{6\pi\eta r_H}{(3r_{\text{solvent}}/2r_H) + (1/(1 + r_{\text{solvent}}/r_H))} \quad (3)$$

Chen and Chen [14] have proposed a useful empirical alternative to this equation.

$$f = \frac{6\pi\eta r_{\text{solute}}}{1 + (0.695(r_{\text{solvent}}/r_{\text{solute}})^{2.234})} \quad (4)$$

In any case, the correction to the friction constant will result in the value “6” being reduced to a value between 4 and 6, with the correction less important for relatively large molecules, i.e., for large r_H values.

To approximately test the validity of the calculated r_H values, obtained from a series of PGSE measurements in our laboratory [15], we compared these values (naively using the constant 6) with the radii, $r_{\text{X-ray}}$, estimated from literature X-ray structures (see Fig. 2 and Table 1). The agreement is perhaps too good given the crude approximations involved, e.g., one obtains $r_{\text{X-ray}}$, by using the volume of the unit cell.

There are a number of obvious- and chemically important-reasons why an r_H value, derived from the Stokes–Einstein equation, might not reflect the solid-state structure of the pure isolated material. These include trapping of a guest in a host, solvent induced aggregation, hydrogen bonding, ion-pairing, etc. However, clearly, temperature effects on solvent viscosity are important. Consequently, it is often useful to simultaneously measure the diffusion constant of a small quantity of a reference compound. The two most often used are tetramethylsilane [16] and

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