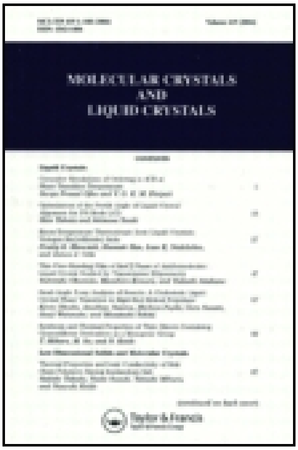

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Analysis of the PFG-SE NMR Experiments in Lyotropic Mesophases: The Hexagonal Case

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The NMR Pulsed Field Gradient Spin-Echo method (PFG-SE) may be conveniently applied to the study of water self-diffusion in lyotropic liquid crystals, giving insight on their molecular organization. The technique has been widely used and mathematical descriptions of the experiments have been worked out which, although simple to visualize, may involve computer calculations rather cumbersome and time consuming. Here we derive a mathematical expression giving the echo attenuation in a PFG-SE experiment which is formally compact and easy to handle by computer simulations technique. Its application to hexagonal mesophases is discussed as an example of how to handle complex situations.

Keywords: NMR, diffusion, lyotropic, hexagonal

INTRODUCTION

We are mainly interested in the application of PFG-SE method[1] to the study of water self-diffusion in lyotropic mesophases, since it offers a way to reveal their molecular organization.[2,3]

The technique consists of a two r.f. pulses Hahn-echo experiment with two identical magnetic field gradient pulses, the first applied between the 90° and the 180° r.f. pulses and the second after 180° r.f. pulse but before the echo.[1] Following the usual notation, the magnetic field gradient pulses have magnitude g, duration δ and separation Δ, and γ indicates the gyromagnetic ratio of the observed nuclei.

Reference 1 gives details concerning the PFG-SE experiment, showing that the significant quantity to be measured is the echo attenuation R, that is the ratio between the echo amplitude in the presence and in absence of the pulse field gradient, respectively, given by:

$$R = R(\delta, \Delta, g) = \int P(r_0)P(r_0, r, \Delta)\cos[\gamma\delta g(r - r_0)]\, dV\, dV_0 \qquad (1)$$

under the assumption that the average displacement during the time interval δ is much lower than the average displacement occurring during the time interval Δ

and there is not net movement of material.[4] Here $P(r_0)$ is the normalized distribution of particles at the time of the first gradient pulse (at $t = 0$) and $P(r_0, r, t)$ is the probability that a particle at r_0 at time zero will have moved to position r at time t. We can possibly obtain information of the diffusion mechanism and on the structural organization by fitting a set of experimental R, measured by PFG-SE technique, to the values calculated through Equation (1), provided we know the function $P(r_0, r, t)$.

The knowledge of the self-correlation function $P(r_0, r, t)$ is, in fact, the crucial point of the problem.

PFG-SE EXPERIMENTS AND WATER SELF-DIFFUSION IN LYOTROPIC MESOPHASES

The evaluation of $P(r_0, r, t)$ certainly appears difficult in lyotropic solutions, due to the complicated variety of structures that, depending on temperature and composition, they may exhibit, e.g. hexagonal, cubic, ribbon and so on.

Diffusion in bulk water may be regarded as taking place in three dimensions, following a simple Brownian motion. In lyotropic solutions this is not the case, and due to obstruction and hydration phenomena, water molecules have a lower translational mobility than in neat water. A further consideration is that lyotropic mesophases consists of numerous and randomly oriented crystalline mono-domains. It is therefore necessary to take into account these factors, in working, through Equation (1), a valuable expression for R.

We may account for the hydration effect by writing, as usual[5]:

$$D = P_b D_b + (1 - P_b) D_f \tag{2}$$

where P_b is the fraction of bounded water, D, D_f and D_b are the observed, self-diffusion coefficient of free and bound water, respectively.

On these assumptions we look for a solution of the diffusion equation:

$$\frac{\partial P(r_0, r, t)}{\partial t} = D\nabla^2 P(r_0, r, t) \tag{3}$$

satisfying the boundary conditions appropriate to the system under consideration. This is equivalent to assuming molecules diffusing randomly, except at the boundaries where they are reflected, and therefore the solution is expected to reflect the obstruction effect.

Finding the solution of Equation (3) is, of course, a formidable task, because of the boundary conditions we have to impose, since the lyotropic mesophases, unless specially prepared, have a poly-domain structure consisting of randomly oriented liquid crystalline mono-domains.

We may however simplify the problem observing that the real experimental situation, where the field gradient g has a defined direction and the mono-domains are randomly oriented, is physically equivalent to one where the single domain has a defined direction and it is the field gradient to have a random distribution.

We therefore refer to a mono-domain defined as the crystalline structure having the same director, and we also assume that during the PFG-SE experiment the diffusing particle will remain in the same domain. This is not a problem if domains are large enough or if the defects at boundaries are assumed not to affect diffuse motions. In a lyotropic liquid crystal sample, normally, it is verified that the domain size is >> $\sqrt{2\Delta D}$.

According to this point of view the echo attenuation R can be expressed by the equation:

$$R = \frac{1}{4\pi} \int P(r_0) P(r_0, r, \Delta) \cos[\gamma\delta g \cdot (r - r_0)] \sin\theta \, d\theta \, d\phi \, dV_0 \, dV \qquad (4)$$

where $1/(4\pi)\sin\theta \, d\theta \, d\phi$ is the probability of g being in the direction defined by θ and ϕ, assuming a randomly oriented distribution of g, with $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$.

$P(r_0)$ and $P(r_0, r, \Delta)$ are the initial molecular distribution and the conditional probability at time Δ, respectively, referred to a single domain.

It is convenient to consider $P(r_0)$ and $P(r_0, r, t)$ in the mono-domain coordinate frame, defined as the frame having one axis coincident with the director, so that the functions $P(r_0)$ and $P(r_0, r, \delta)$ are independent of the angular variables (θ, ϕ), defining g [i.e. $g \equiv (g \sin\theta \cos\phi, g \sin\theta \sin\phi, g \cos\theta)$].

By integration over θ and ϕ we obtain*:

$$R = \int P(r_0) P(r_0, r, \Delta) \frac{\sin(\gamma\delta g|r - r_0|)}{\gamma\delta g|r - r_0|} \, dV \, dV_0 \qquad (5)$$

An advantage of Equation (5) is that the evaluation of R entails the knowledge of the self-correlation function just for a single mono-domain since, by angular averaging, we have accounted for their random distribution.

When $P(r_0, r, t)$ is mathematically available, the integration (5) can be, in principle, worked out. For example, using the known expression[7,8] for $P(r_0, r, t)$

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*Equation (5) follows from[6]:

$$\int_0^\pi \int_0^{2\pi} f(a\cos\theta + b\sin\theta\cos\phi + c\sin\theta\sin\phi)\sin\theta \, d\theta \, d\phi$$

$$= 2\pi \int_0^\pi f(A\cos\theta)\sin\theta \, d\theta = 2\pi \int_{-1}^{1} f(At) \, dt$$

$A = \sqrt{a^2 + b^2 + c^2}$ and therefore:

$$\int_0^\pi \int_0^{2\pi} \cos\gamma\delta g[(x - x_0)\sin\theta\cos\phi + (y - y_0)\sin\theta\sin\phi + (z - z_0)\cos\theta]\sin\theta \, d\theta \, d\phi$$

$$= 2\pi \int_{-1}^{1} \cos(\gamma\delta g|r - r_0|t) \, dt = 4\pi \frac{\sin\gamma\delta g|r - r_0|}{\gamma \, dg|r - r_0|}$$

describing the diffusion between thin layers and inside a cylinder with negligible radius, two situations referred to as two dimensional and one dimensional diffusion, it is straightforward but tedious to obtain, respectively:

$$R_{2d} = 1 + \sum_{n=1}^{\infty} (-1)^n \frac{n!}{(2n+1)!} 4^n (K\Delta D)^n \tag{6}$$

and

$$R_{1d} = 1 + \sum_{n=1}^{\infty} (-1)^n \frac{1}{n!(2n+1)} (K\Delta D)^n \tag{7}$$

where $K = (\gamma\delta g)^2$

The same results have already been obtained by a more direct analysis.[9,10]

The real utility of Equation (5) is when the mathematical expression of $P(r_0, r, \Delta)$ is not available. In many situations, in fact, even when the structure of the system is known, the differential equation (with boundary conditions) cannot be resolved, and the mathematical analysis of the PFG-SE experiment can be handled only numerically, by computer applying appropriate simulation technique. This is the case of water diffusion in hexagonal mesophases, a problem that, in our knowledge, has never been solved satisfactorily.

SELF-DIFFUSION IN HEXAGONAL MESOPHASE

Here the mono-domain structure consists of an hexagonal array of polar cylinders, with the polar heads on the surface and the hydrocarbon tails turning towards the cylinder axis. This long axis is also the mono-domain director. Transverse dimensions are of the order of some tens of Å. In potassium palmitate, for example, the cylinder diameter is about 35 Å, and the nearest neighbor distance is in the 50–60 Å range, approximately, depending on the water content.[11] Although the hexagonal array restricts the water diffusion, a molecule can move, during the time Δ, distances longer than the transverse dimensions. Here it is impossible to find a mathematical expression for $P(r_0, r, t)$. It is however possible to evaluate the spin-echo attenuation R by a computer numerical simulation of the self-correlation function, a problem that, as far as we know, has never been discussed for hexagonal lyotropic liquid crystals.

By selecting at random the initial position r_0, we generate a simulation of the Brownian motion of the particles, consisting of jumps by steps of fixed length, in random directions and we calculate the final position r reached at the time Δ. Reflections at the walls of the hexagonal array are accounted by using the cellular automata method.[12] By multiple repetition of the procedure we build a significant statistical ensemble. We have assumed, for the jump length l a value of 2 Å, typical of bulk water, much smaller than the dimensions of obstacles restricting the diffusion, a condition to be fulfilled for our analysis to be correct. Details of the method and results are discussed elsewhere.[13,14]

For a given value of the ratio d/L, where d and L are the diameter and the nearest neighbors distance of the cylinders, respectively, we obtain numerically simulated data for R. As a result we find that any set of data, corresponding to a given d/L value in the range 0–1, falls between the two lines describing capillary and isotropic unrestricted diffusion, coinciding with the first one for $d/L = 1$ (hexagonal close packed array) and approximating the second one for $d/L \Rightarrow 0$, as is expected on the basis of simple physical considerations.

In order to avoid confusing superimposition, Figure 1 reports simulated data for only three values of the ratio d/L. In order to simulate a realistic situation (e.g. potassium palmitate) we have assumed $d = 35$ Å and a value of 40 or 50 or 60 Å for L.

An important point to be noted is that the curved behavior on ln R would be difficult to observe experimentally, since the value of $d/L \simeq 1$ are not available, and, for $d/L \leq 0.8$ such curvature, if any, would correspond to small values of ln R affected, therefore, by low accuracy.

Finally, in order to investigate the usefulness of our approach we have selected a solution of potassium palmitate, the structure of which has been determined by X-ray as being hexagonal with $L = 38$ Å, $d = 58$ Å at temperature of 100°C and concentration of about 34% in weight of water.[11]

In Figure 2 the experimental value of R is shown measured by PFG-SE technique, on a sample at the above condition. In the same figure are reported R values calculated by Equation (5) using simulation technique, as described before, selecting $d = 38$ Å and $L = 58$ Å, for different values of D. Experimental and simulated data coincide when $D = 4.9\ 10^{-6}$ cm^2 sec^{-1}.

From the slope we find $D_a = 3.9\ 10^{-5}$ cm^2 sec^{-1} and, therefore, a value $f = D_a/D = 0.80$, for the obstruction factor f.[3,15] This factor, as usual, reflects the microstructure of the hexagonal entanglement.

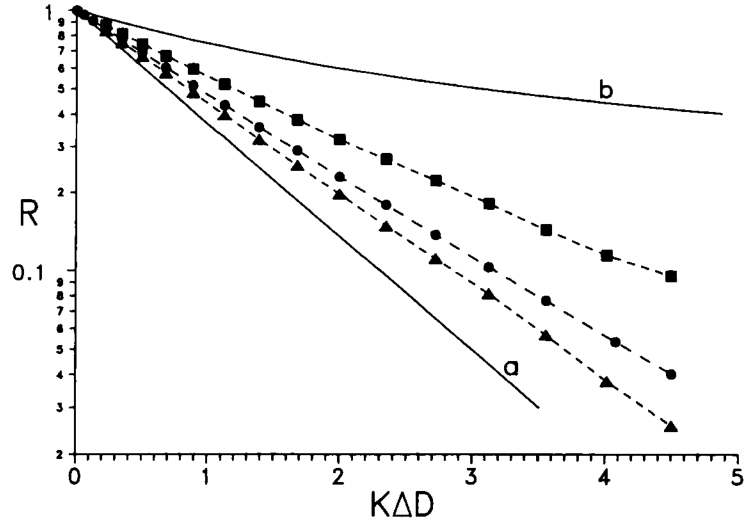

FIGURE 1 (a) and (b) refer to unrestricted and capillary [Equation (10)] diffusion, respectively. (■), (●) and (▲) are simulated data for hexagonal arrays with d/L equal to 7/8 (35 Å/40 Å), 7/10 (35 Å/50 Å) and 7/12 (35 Å/60 Å) respectively.

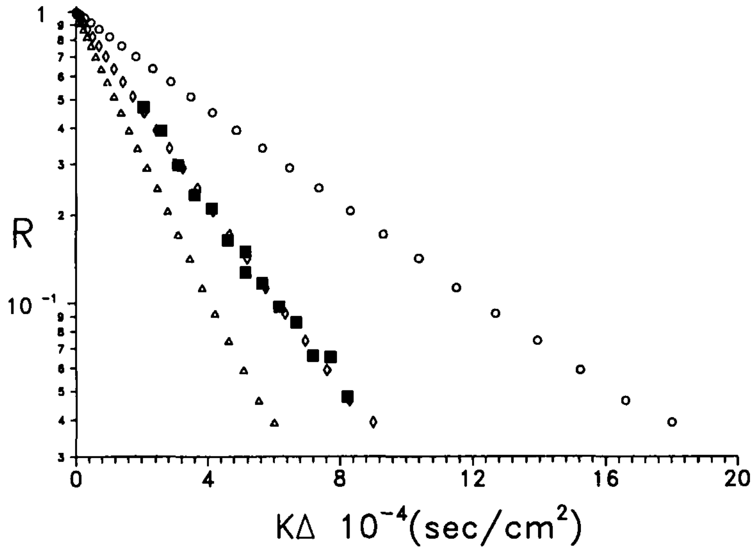

FIGURE 2 (■) refers to experimental values of palmitate potassium sample (see text). (○), (◇) and (△) are simulated measurements for hexagonal arrays with d/L equal to 38 Å/58 Å and with D equal to 2.5 10^{-6}, 4.9 10^{-6} and 7.5 10^{-6}, respectively.

CONCLUSIONS

We have derived an expression describing the PFG-SE in lyotropic solution with poly-domain structure. In addition to confirming results already obtained by a different approach, our analysis seems to be particularly useful in interpreting the PFG-SE experiment on systems, for which an analytical solution of the diffusion equation is not available.

In particular it can be applied to the study of water diffusion in hexagonal mesophases, as well as in mesophases with complex crystalline structure. Evidence of the potential of the method is provided by the study of diffusion in hexagonal potassium palmitate which is discussed and commented.

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