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● *Contributed Paper*

SELF-DIFFUSION OF WATER AND OIL IN PEANUTS INVESTIGATED BY PFG NMR

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Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) has been used to study self-diffusion characteristics of water and oil in natural peanuts and in peanuts saturated with water. From the dependence on diffusion time of the echo decay due to diffusion, regions of completely restricted diffusion for the oil molecules were identified. The mean size and size distribution function of these regions were obtained. Combined analysis of diffusion data for peanuts with natural moisture content and for water saturated peanuts shows the cellular nature of these regions. The cell structure, consisting of a cell cavity surrounded by a double membrane was identified. © 1998 Elsevier Science Inc.

Keywords: **Pulsed-field gradient; Restricted diffusion; Porous media; Cell structure.**

INTRODUCTION

The application of pulsed field gradient (PFG) nuclear magnetic resonance (NMR) to the investigation of biological systems is motivated by the successes of this technique for study of the structure of porous media,[1] as well as of characteristics of molecular mobility in heterogeneous systems.[2] Thus, PFG NMR can give unique information about structure and dimensions of the biological objects under investigation.[3–8] The main purpose of the present work was the investigation of the cell structure of peanuts, using strong magnetic field gradients.

The shelled peanuts (*Arachis hypogea*) used for investigations were tightly packed into a glass tube and sealed. The initial water content, determined by weight, was 6%. To obtain additional information, a sample of oil pressed from the peanuts and a sample of peanuts saturated with water to 35% were investigated. Saturation was accomplished by keeping the peanuts in water at room temperature for 24 h.

Measurements were performed on home-built equipment working at a proton frequency of 64 MHz and with a maximum PFG of 200 T/m. A stimulated-echo pulse sequence was used. Diffusion time, t_d, was varied from 5 to 3000 ms and gradient pulse duration, δ, from 0.1 to 0.3 ms; thus, the conditions for the short-gradient pulse limit were fulfilled. These parameters provide spatial resolution, $q = (\gamma\delta g)^{-1}$, down to 0.07 μm. Temperature was kept at 30 ± 0.5°C. The decay of echo amplitude due to diffusion and average self-diffusion coefficient (SDC) were the measured values. Average SDC was determined from the initial slopes of the decays plotted against $(\gamma\delta g)^2$. The precision of SDC's and component fractions is 5–15%.

EXPERIMENTS

The sample of pure peanut oil gave uni-exponential diffusion decay over two decades, independent of diffusion time. Thus, diffusion in peanut oil is characterized by a single SDC equal to $1.34 \pm 0.06 \times 10^{-11}$ m^{2}s^{-1} at 30°C. Typical experimental diffusion decay results are shown as functions of $(\gamma\delta g)^2$ for five t_d values in Fig. 1.

The main feature of the observed echo decay due to diffusion in peanuts is the transition from uni-exponential decay at short t_d to multi-exponential form at long t_d. For $t_d > 200$ ms, normalized decay does not depend on diffusion time, indicating completely restricted diffusion.[4] The initial slope is constant for $t_d > 120$ ms, giving $D_s(t_d) \propto t_d^{-1}$, as shown in Curve 1 of Fig. 2. Applying the equation[2]:

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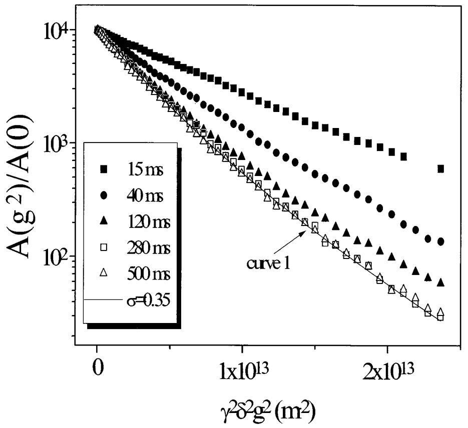

Fig. 1. The dependence of echo attenuation due to diffusion on diffusion time t_d in peanuts. Curve 1 is for a log-normal distribution function with $\sigma = 0.35$.

$$D^{eff}(t_d) = \frac{D_0 D_s(t_d)}{D_0 - D_s(t_d)} \tag{1}$$

shows $D^{ef}(t_d) \propto t_d^{-1}$ (Curve 2, Fig. 2) for the whole range of diffusion times used. From Einstein's relation, the size of the regions of restricted diffusion is 1.2 ± 0.1 μm.

Even for media with a single size of restricted diffusion cell, multi-exponential diffusion decay is observed. However, the deviation from simple exponential form is displayed only in the third decade of the normalized echo decay. In our case (Fig. 1) non-exponentiality is observed in the first decade. It can be explained by a distribution of restricted diffusion cell sizes.

Our computer calculations have shown that the multiexponential decay obtained at long diffusion times, where the whole population of molecules is in the regime of completely restricted diffusion, can be fitted well by a log-normal distribution function with $\sigma = 0.35 \pm 0.02$. Thus, the conclusion about bimodal distribution function obtained in the work of Maphossa and Halse for peanuts is not verified, and neither is the minimum size of 0.1 μm for restricted diffusion cells, with 40% of the signal. Our results show a minimum size of 0.95 μm with a population of 10%.

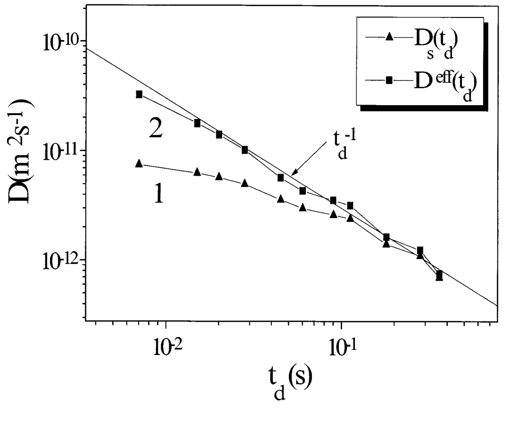

Fig. 2. Dependence of the measured average SDC D_s (Curve 1) and SDC D^{eff} computed from Eq. (1) (Curve 2) on diffusion time t_d for peanuts.

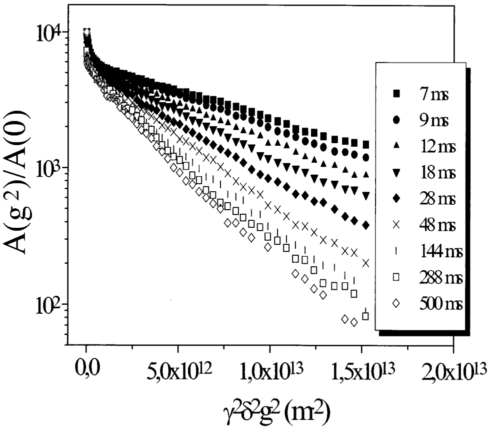

Fig. 3. The dependence of echo attenuation due to diffusion on diffusion times t_d in 35% water-saturated peanuts.

The water content of the natural peanut is so little that the component with the water SDC is not displayed.

To check the hypothesis of the diffusion of oil molecules with diffusion restricted to cells with a narrow range of sizes in peanuts, we carried out additional investigations of water and oil diffusion in water-saturated peanut samples. The normalized echo attenuations obtained in the 35% water-saturated samples for t_d from 7 to 500 ms and the PFG g = 200 T/m are shown in Fig. 3. In the vicinity of the minimum accessible diffusion time, the attenuations have complicated non-exponential forms. These decays can be decomposed into three exponential components with different SDC's.

The dependence on diffusion time t_d of the three components is presented in Fig. 4. As can be seen, the SDC of the a-component has the characteristic of completely restricted diffusion, $D_s(t_d) \propto t_d^{-1}$ for $t_d > 120$ ms. Just as for the natural peanut, the lack of t_d-dependence at long times indicates strict confinement of the oil to diffusion cells, indicating the absence of significant membrane permeability to oil for experimental times. The value of D_d for short diffusion times corresponds roughly with the SDC value of pure peanut oil. This fact permits us to treat the a-component as the oil molecules in the system. Moreover, the calculated size of the re-

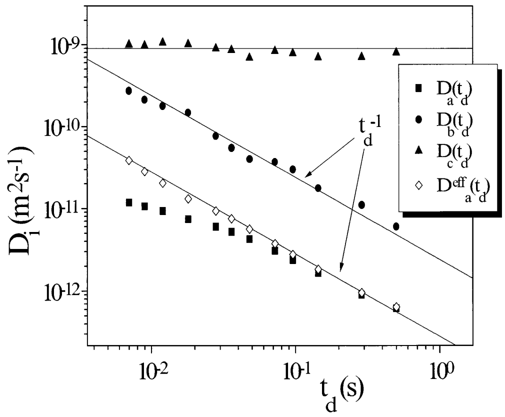

Fig. 4. The dependence of the SDC of a-, b-, and c-components (D_a, D_b, and D_c), obtained by decomposition of experimental echo attenuations in the water-saturated peanuts.

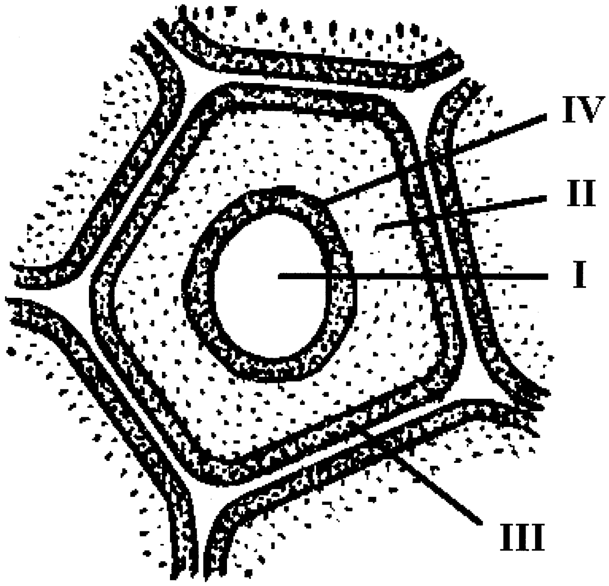

Fig. 5. The model structure of peanut cells: I = cell cavity; II = amorphous matrix; III = external membrane film; IV = internal membrane film.

stricted diffusion cells is 1.2 ± 0.1 μm, which corresponds to the average cell dimensions obtained for natural peanuts with 6% moisture. The rise of D_a in comparison with pure oil SDC for short t_d shows the presence of permeability of the oil-field cavity membrane for water, which influences oil translational characteristics. Therefore, it is possible to draw an important conclusion that the cell membrane is not permeable for oil and is able to pass water.

The SDC of the b-components and c-components, D_b and D_c, are within an order of magnitude of the SDC of pure water (2.60×10^{-9} m/s at 30°C). We have $D_b(t_d) \propto t_d^{-1}$ for the entire accessible range of t_d, beginning with 7 ms. The restricted diffusion cell size for water is 3.0 ± 0.2 μm, a little over twice the size of that for the oil molecules. The SDC of the c-component is independent of diffusion time. In this case, diffusion is not restricted to diffusion cells. However, diffusion may be restricted to somewhat tortuous paths, accounting for D_c being somewhat less than the SDC of bulk water at 30°C.

All the experimental data can be explained by the following structure model[9] for peanuts (Fig. 5). The peanut cell is composed of a 1.2-μm diameter oil-field cavity surrounded by a double membrane. The completely restricted diffusion for oil molecules confirms that the inner membrane is not permeable to oil molecules in the time interval investigated.

RESULTS

The experimental data for water-saturated peanuts show an average diffusion cell size to be 3.0 ± 0.2 μm. This region is the space formed by the external membrane. Thus, the distance between inner and outer cell membranes is about one micrometer. It is important to point out that the outer membrane is permeable to water molecules for very long diffusion times but not for the experimental time interval. The observed rise of oil molecules mobility for the water-saturated sample shows the water permeability of the inner membrane. The presence of another water phase for the SDC being independent of diffusion time indicates that the extracellular water can diffuse long distances. Restriction to somewhat tortuous paths appears to reduce the SDC to a value several times smaller than that of bulk water. This model is confirmed by available information[9] about cell structure.

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