Eur Biophys J (1990) 19:25–30

European Biophysics Journal

NMR-investigation of restricted self-diffusion of oil in rape seeds

G. Fleischer[1], **V. D. Skirda**[2], **and A. Werner**[3]

[1] Karl-Marx-Universität Leipzig, Sektion Physik, Linnéstrasse 5, DDR-7010 Leipzig, German Democratic Republic
[2] Kazan State University, Department of Physics, Lenina 18, SU-420008 Kazan, USSR
[3] Ingenieurhochschule Berlin-Wartenberg, WB Physik, Postfach 56, DDR-1120 Berlin, German Democratic Republic

Received February 8, 1990/Accepted in revised form June 20, 1990

Abstract. The self-diffusion of oil and water in rape seeds (*Brassica napus* L.) was measured with the NMR pulsed field gradient technique. The self-diffusion of oil was found to be completely restricted for diffusion times $\Delta > 30$ ms. The experiments could be explained in terms of the model of diffusion within spherical droplets and a Gaussian mass distribution of the droplet radii. The mean droplet radius was found to be about 0.7 μm; this value decreased somewhat with increasing moisture content of the seeds. The experiments could also be explained with a Gaussian number distribution of droplet radii and a fraction of immobile protons in the NMR signal of 5 ... 10%, possibly arising from lipid protons. Though the transverse nuclear magnetic relaxation decay of the oil protons is not a single exponential we observe one uniform diffusive mobility for the oil molecules. The water self-diffusion coefficient at maximum moisture content of about 40% was determined to be $4.2 \cdot 10^{-10}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ which is typical for swollen polymer-solvent systems at such a concentration.

Key words: NMR pulsed field gradient technique – Self-diffusion – Oil – Rape seeds

Introduction

The characterization of water and other compartments in biological systems with physical methods is of great practical importance. Nuclear magnetic resonance, widely applied in investigating molecular systems, is a valuable tool for characterizing structure and dynamics of biological systems. For example, NMR may be used to determine the water content in agricultural and other biological products, and for this purpose it is necessary to know the NMR behaviour of all the constituents of these products.

Today the NMR pulsed field gradient technique (NMR-PFGT) is widely used to investigate molecular transport in systems such as, for example, pure liquids and mixtures, polymers, porous solids and also biological systems. Many comprehensive review articles exist (von Meerwall 1983; Callaghan 1984; Stilbs 1987; Maklakov 1987; Kärger et al. 1988). With the NMR pulsed field gradient technique the self-diffusion of mobile proton-containing species can be measured, and the self-diffusion coefficient is intimately connected with the structure of the system. Callaghan et al. (1983) have, for example, investigated fat and water self-diffusion in cheese and observed restricted diffusion of fat within droplets. The mean droplet size could be immediately determined from the NMR experiment. In a similar fashion we have investigated oil and water diffusion in rape seeds of different varieties. The ultimate aim of this work is the elucidation of the NMR behaviour of oil and water in the rape seeds to ensure a precise routine determination of water content from NMR measurements, but the NMR-PFGT technique shows other interesting results which are also presented in this paper.

NMR pulsed field gradient technique

NMR self-diffusion measurements are based on local differences in the Larmor frequencies, when applying a spatially varying magnetic field (field gradients), which result in an attenuation of the spin echo amplitude in addition to nuclear magnetic relaxation if the spins have changed their positions during the spin echo experiment.

Applying two field gradient pulses of duration δ, intensity g and separation Δ in the interval between the $(\pi/2)$- and π-pulses, and the π-pulse and the echo, respectively, the attenuation of the spin echo is obtained by integration over all spin positions z (where the spins are located during the first gradient pulse), and z_2, (where the spins are located at the second gradient pulse). Taking into account that the individual spin contributes to the signal only by the cosine of the phase shift $\Delta\phi$ effected by the two field gradient pulses one thus obtains

$$\psi(\Delta, \delta g) = \iint P(z_1)\, P(z_2, z_1, \Delta) \cos[\gamma \delta g (z_1 - z_2)]\, \mathrm{d}z_1\, \mathrm{d}z_2 \tag{1}$$

Offprint requests to: G. Fleischer

$P(z_1, z_2, \Delta)\,dz_2$ is the probability that a spin located at z_1 has moved to z_2 (within the interval dz_2) after the time Δ. $P(z_1)\,dz_1$ is the probability of finding the spin in the interval dz_1 at z_1 during the first gradient pulse. In a homogeneous medium $P(z_1)=\text{const.}$, and the solution $P(z_1, z_2, \Delta)$ of Fick's second law with the initial probability distribution $\delta(z_1)$ is straightforwardly found to be

$$P(z_1, z_2, \Delta)=\frac{1}{(4\pi D\Delta)^{0.5}}\exp\left[-\frac{(z_2-z_1)^2}{4D\Delta}\right]. \tag{2}$$

D is the self-diffusion coefficient. Inserting (2) into (1) one obtains

$$\psi=\exp(-\gamma^2\delta^2 g^2 D\Delta) \tag{3}$$

which via Einstein's relation

$$\langle z(\Delta)^2\rangle=2D\Delta \tag{4}$$

may easily be transformed into the expression

$$\psi=\exp(-\gamma^2\delta^2 g^2\langle z(\Delta)^2\rangle/2), \tag{5}$$

which directly relates the echo attenuation to the mean square displacement of the spins in the direction of the pulsed field gradients.

As soon as molecular propagation is not governed by a Gaussian distribution of the type of (2), (3) no longer holds and the echo attenuation must be determined by starting directly with (1). This is the situation in dealing with the oil diffusion in rape seeds. The oil is dispersed in the seed within which the oil droplets are considered as spheres. The restricted diffusion within spheres of radius R has been treated by Tanner and Stejskal (1968). In the asymptotic limit of long diffusion times, at $\Delta D \gg R^2$, the diffusion is completely restricted by the rejection of the oil molecules from the surface of the droplets, and for ψ one obtains

$$\psi=\frac{9[\gamma\delta g R\cos(\gamma\delta g R)-\sin(\gamma\delta g R)]^2}{(\gamma\delta g R)^6}. \tag{6}$$

Equation (6) can be well approximated by

$$\psi=\exp(-\gamma^2\delta^2 g^2 R^2/5) \tag{7}$$

up to an echo attenuation of about 0.15.

If one measures in the region of restricted diffusion, i.e. at $\Delta \gg R^2/D$, using (3) one gets from the echo attenuation an experimental (or apparent) self-diffusion coefficient D_{exp} which depends on R^2 and the diffusion time Δ as

$$D_{\text{exp}}=R^2/5\Delta, \tag{8}$$

i.e. D_{exp} decreases with Δ.

If there is a distribution $p(x)$ of physical parameters x which leads to a distribution of diffusion coefficients or distances of diffusion barriers, the echo attenuation becomes a superposition of exponentials in the form

$$\psi=\frac{\int p(x)\exp[-\gamma^2\delta^2 g^2 D(x)\Delta]\,dx}{\int p(x)\,dx}. \tag{9}$$

$p(x)\,dx$ is the mass portion of species with the property x in the range between x and $x+dx$. x can be the self-diffusion coefficient itself ($D(x)=x=D$), the distance R of diffusion barriers, its square R^2 or other properties controlling the diffusion process. We have to use the mass portion because the contribution of each species to the signal is proportional to its number of spins (hydrogen nuclei) and hence to its mass.

The initial slope of the echo attenuation plot $\ln\psi$ vs. $(\delta g)^2$ gives the mass-average of the diffusion coefficient or the square of the barrier distances (here the droplet radii):

$$-\left.\frac{d\ln\psi}{d(\gamma^2\delta^2 g^2\Delta)}\right|_{(\delta g)^2\to 0}=\int p(x)\,D(x)\,dx \tag{10}$$

$$=\bar{D}=\bar{R}^2/5\Delta \tag{10a}$$

In this work, we have tested the following distributions: (*i*) a log-normal distribution of diffusion coefficients D

$$p(D)\,dD\sim\exp\left(-\frac{\ln^2 D/D_0}{2\sigma_D^2}\right)\frac{dD}{D} \tag{11}$$

which is equal to a distribution of R^2 in the case of restricted diffusion (see (8)) like

$$p(R^2)\,dR^2\sim\exp\left[-\frac{\ln^2(R^2/R_0^2)}{2\sigma_D^2}\right]\frac{dR^2}{R^2}. \tag{12}$$

For $\bar{R}^2$ we get from (10)

$$\bar{R}^2=R_0^2\exp(+\sigma_D^2/2) \tag{13}$$

(*ii*) a normal (Gaussian) mass distribution of radii around R_0

$$p(R)\,dR\sim\exp\left[-\frac{(R-R_0)^2}{\sigma_R^2}\right]dR \tag{14}$$

with which (9) can be solved analytically:

$$\psi=(1+\alpha^2\sigma_R^2)^{-0.5}\exp\left(-\frac{\alpha^2 R_0^2}{1+\alpha^2\sigma_R^2}\right) \tag{15}$$

and

$$\bar{R}^2=R_0^2+\sigma_R^2/2. \tag{16}$$

(*iii*) a Gaussian number distribution of radii around R_0. Then the mass distribution is

$$p(R)\,dR\sim R^3\exp\left[-\frac{(R-R_0)^2}{\sigma_R^2}\right]dR \tag{17}$$

and the analytical solution of (9) is

$$\psi=\frac{2R_0^2+3\sigma_R^2(1+\alpha^2\sigma_R^2)}{(2R_0^2+3\sigma_R^2)(1+\alpha^2\sigma_R^2)^{3.5}}\exp\left(-\frac{\alpha^2 R_0^2}{1+\alpha^2\sigma_R^2}\right) \tag{18}$$

and

$$\bar{R}^2=R_0^2+0.5\,\sigma_R^2\left(7-\frac{2}{1+2R_0^2/3\sigma_R^2}\right). \tag{19}$$

σ generally is the distribution width and $\alpha^2=\gamma^2\delta^2 g^2/5$.

The distributions (*ii*) and (*iii*) are already used in the work of Callaghan et al. (1983) for fat diffusion in cheese. As we shall see later, in the spin echo signal of the rape

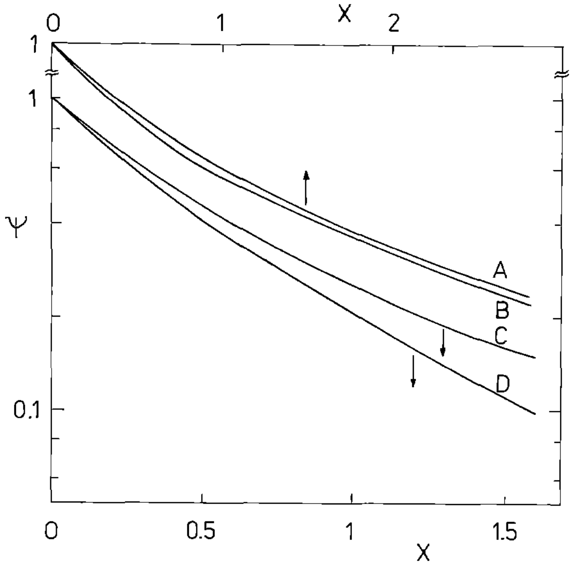

Fig. 1. Echo attenuation ψ calculated theoretically with (9) and distribution (*i*) (*A*), distribution (*ii*) (*B*), distribution (*iii*) (*D*) and calculated with (20) and distribution (*iii*) (*C*). The parameters are $\sigma_D^2=1.0$, $\sigma_R^2/R_0^2=0.3$ and $A=0.05$. $X=\gamma^2\delta^2g^2R_0^2/5$ or $\gamma^2\delta^2g^2D_0\Delta$

seeds there seems to be a portion of immobile protons which, however, have such long nuclear magnetic relaxation times that they are present in the spin echo in our experiments. This leads for the echo attenuation to

$$\psi = A + (1-A)\frac{\int p(x)\exp(-g^2\delta^2g^2D\Delta)\,\mathrm{d}x}{\int p(x)\,\mathrm{d}x}. \tag{20}$$

In Fig. 1 we have shown some typical echo attenuation plots calculated with the above mentioned distributions. As can be seen from this figure, the form of the plots differs only slightly for the curves A, B, and C. In Fig. 1, parameters σ and A were chosen to give a good fit to the experimental results, see below. The curvature of the plots increases with increasing σ and A.

In the model used the barriers (the surfaces of the oil droplets) were assumed to be impenetrable for the oil molecules. If this is not the case, the experimental diffusion coefficient for times going to infinity $D^{(\infty)}$ does not assymptotically go to zero due to the flux $j=p\,\Delta c$ of oil through the barriers. Δc is the difference of oil concentration between the oil in the droplets and the oil outside the droplets. From $D(0)$ of free diffusion at $\Delta\to 0$ and $D^{(\infty)}$ one can estimate the barrier permeability p from

$$D^{(\infty)} = \frac{D(0)}{1+D(0)/p\,a} \tag{21}$$

with the barrier distances a (Tanner 1978; von Meerwall and Ferguson 1981).

Experimental

The apparatus and the measuring technique has been described in detail elsewhere (Fleischer et al. 1985; Maklakov et al. 1987). The stimulated echo pulse sequence was used with $\tau_1=2$ ms, the diffusion time Δ was varied between 3.5 and 1000 ms and g from 0 up to about 50 T/m, δ was kept constant. All measurements were carried out at room temperature, one sample was also measured at $T=65$ °C (*Sollux*).

Three varieties of rape seeds (*Brassica napus* L.) *Sollux*, *Maras* and *Marex* were investigated. The seeds were either dried in a desiccator over P_2O_2 or held in a humid atmosphere with a particular relative humidity to achieve a moisture content in the seeds of about 12% (determined gravimetrically). For the measurements the seeds were sealed in glass tubes with 7 mm outer diameter. The self-diffusion coefficient of the water in the rape seeds was determined only for maximum humidity which was about 40% water/dry seed.

The apparent self-diffusion coefficient D_{exp} is determined from the initial slope of the echo attenuation plot, the radius R_0 and distribution width σ_R according to distribution (*ii*), (14), were determined by fitting the experimental data for diffusion times $\Delta > 30$ ms with the theoretically calculated ψ of (15). The experimental error of R_0 is in the order of 10%, that of σ_R about 20 ... 30%.

Results

In Fig. 2 a typical echo attenuation plot of oil in rape seeds is shown. The plot is non-exponential, and with the exception of low diffusion times $\Delta < 30$ ms the echo attenuation does not depend on the diffusion time Δ. In Fig. 3 ψ is plotted versus the diffusion time Δ at two constant δg-values. In Fig. 4 the mass-averaged self-diffusion coefficient $D_{\text{exp}}\,(=\bar{D})$ determined from the initial slope of the experimental echo attenuation is shown as a function of the diffusion time Δ. Beginning at $\Delta\approx 30$ ms, D_{exp} is inversely proportional to Δ. For short diffusion times the crossover to free diffusion is well seen. The self-diffusion coefficient of pure oil was measured as $1.6\cdot 10^{-11}\ \text{m}^2\,\text{s}^{-1}$ for variety *Marex* and $1.2\cdot 10^{-11}\ \text{m}^2\,\text{s}^{-1}$ for variety *Sollux*.

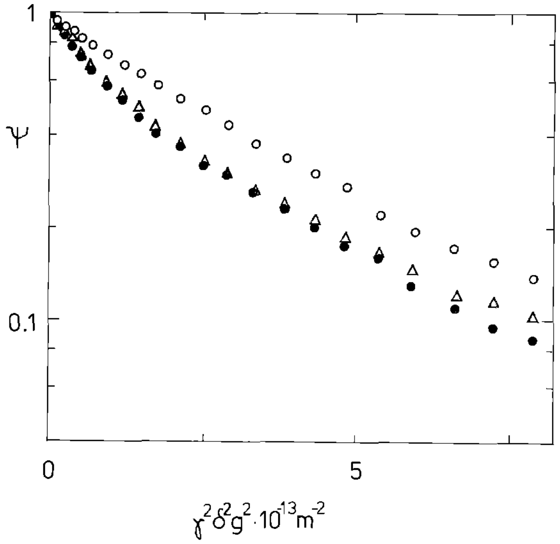

Fig. 2. Experimentally observed echo attenuations for rape seed of variety "*Maras*", moisture content <1%, at diffusion times $\Delta=13$ ms (○), 100 ms (△) and 600 ms (●)

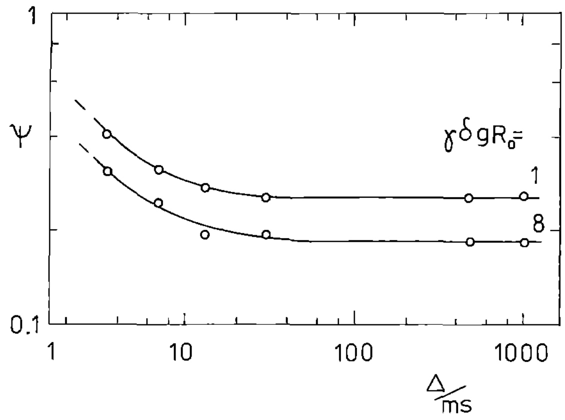

Fig. 3. Echo attenuation as a function of Δ for $\gamma\,\delta\,g\,R_0 = 1$ and 8, resp., for variety "*Sollux*", moisture content 12.9%, at $T = 65\,^\circ\mathrm{C}$

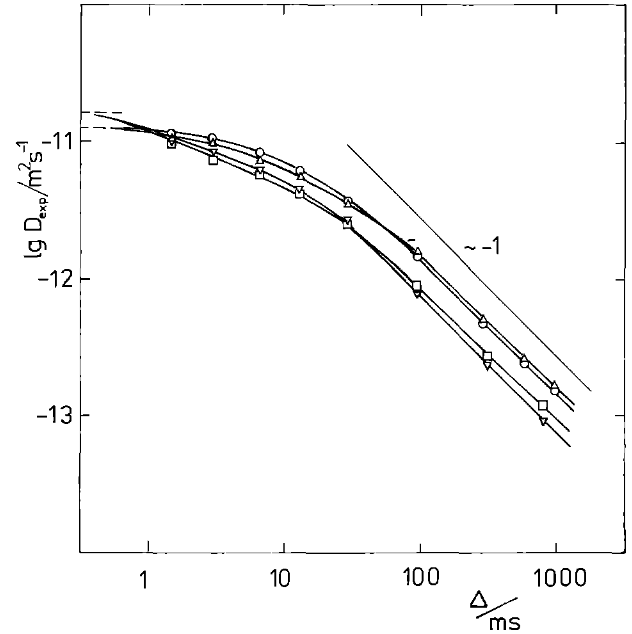

Fig. 4. $\lg D_{\mathrm{exp}}$ vs. $\lg \Delta$ for different varieties of rape seeds. At the ordinate the self-diffusion coefficients of free oil D_0 are indicated by dashed lines. △: *Sollux*, moisture content 3.5%; ○: *Sollux*, moisture content 12.9%; □: *Marex*, moisture content 3.2%; ▽: *Marex*, moisture content 13.2%

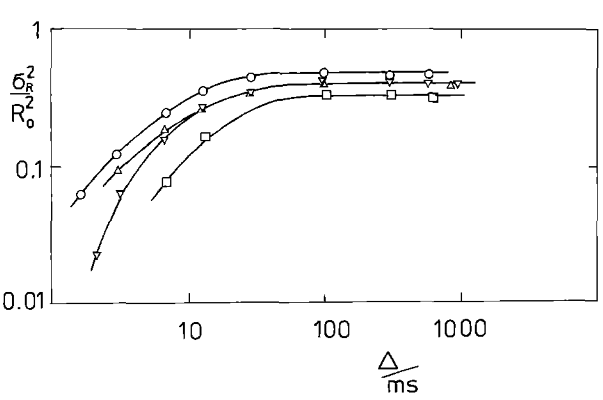

Fig. 5. $\lg(\sigma_R^2/R_0^2)$ according to distribution (*ii*) vs $\lg \Delta$. Symbols as in Fig. 4

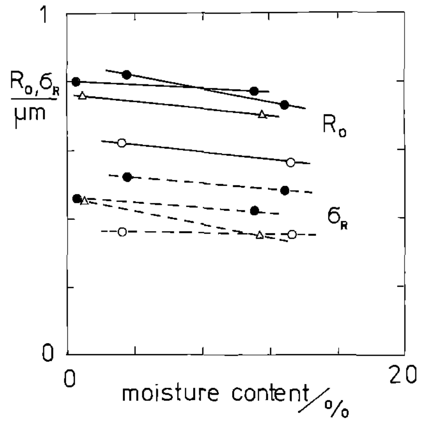

Fig. 6. Radius R_0 and distribution width σ_R of oil droplets for three varieties of rape seeds "*Sollux*" (○), "*Marex*" (●) and "*Maras*" (△) as a function of moisture content

Three main conclusions can be drawn: (*i*) at $\Delta > 30$ ms ψ no longer depends on Δ, the diffusion is completely restricted, the echo attenuation is only determined by the diffusion barriers, (*ii*) the barriers are found to be impenetrable because $D^{(\infty)}$ for $\Delta \to \infty$ goes to zero, see also (21), and (*iii*) there is a non-exponential echo attenuation arising from a distribution of barrier spacings.

The curvature of the echo attenuation plot cannot be interpreted as being due to restricted diffusion. In the case of diffusion in one dimension (through an ensemble of randomly oriented capillaries) or in two dimensions (in an ensemble of randomly oriented planes) the echo attenuation plot $\ln \psi$ vs. $(\delta g)^2$ becomes upwards concave, and the diffusion of water in endosperm tissue of wheat grains (Callaghan et al. 1979) and liquid crystals can be explained by such a diffusion mechanism with one single diffusion coefficient. In the case of oil in rape seeds we must assume that the oil is distributed in droplets within the seeds. The restricted diffusion of species within spherical droplets shows for long diffusion times an echo attenuation plot slightly upwards convex (6), therefore the assumption of a distribution of radii is inevitable.

In our experiments, in almost all cases the experimentally determined echo attenuations are equally well described by the distributions (*i*) and (*ii*) and (9). We have used distribution (ii) with which ψ can be obtained analytically, see (15). From fitting the calculated ψ to the experimentally determined ψ we obtain R_0 and σ_R. In Fig. 5 σ_R^2/R_0^2 is shown as a function of the diffusion time Δ. In the case of restricted diffusion, at $\Delta \gg 30$ ms, the distribution width remains constant and represents only the distribution of radii, i.e. the topology of the system. In contrast, at the lower end of the time scale the distribution width decreases to zero, to the value of free oil diffusion. Though the oil of the rape seeds is a mixture of triglycerides with different fatty acid composition, the echo attenuation of pure oil is exponential down to 1%. We observe only one averaged self-diffusion coefficient.

In Fig. 6 the mean radii R_0 and distribution widths σ_R are displayed. R_0 lies in the range between 0.6 and 0.8 μm with a distribution width of 0.35 to 0.50 μm. Both R_0 and σ_R slightly decrease with increasing moisture content, and (mainly) R_0 depends on the variety of rape. The diffusion barriers for the oil self-diffusion are not the cell-walls. The oil droplets are much smaller than the size of the cells.

Now we shall discuss the distribution width $p(x)$ in more detail. From experimental results, the distribution (*ii*) with a Gaussian distribution of mass of spherical droplets with radii between R and $R+\mathrm{d}R$ is appropriate to describe the oil distribution in the rape seeds. From this distribution we can calculate the number $n(R)$ of spherical droplets with radius R between R and $R+\mathrm{d}R$

$$n(R) \sim \frac{p(R)}{R^3} \sim \frac{\exp[-(R-R_0)^2/\sigma_R^2]}{R^3}. \tag{22}$$

The distribution $n(R)$ is shown in Fig. 7. Our interpretation of the form of the echo attenuation plot implies a large content of very small oil droplets since $n(R)$ dramatically increases for $R \leq 200$ nm[1], or more generally, there is a fraction on non-diffusing protons in the signal. Such small oil droplets show only a negligible echo attenuation owing to diffusion.

The immobile part can be directly involved in the interpretation of the experimentally observed echo attenuation by using (20) and distribution (*iii*). This means a Gaussian number distribution of droplets of radius R around R_0 and additionally a content of immobile oil or another non-diffusing fraction of protons in the rape seeds with nuclear magnetic relaxation times comparable with those of the diffusing oil. This model seems to be most realistic from a physical point of view. From Fig. 1 one can see that this model describes the experiments equally well. Unfortunately we now have three adjustable parameters, R_0, σ and A which cannot be determined from the NMR-PFGT experiment alone. The curvature of the echo attenuation plot at large attenuations is most sensitive to the immobile fraction, but the experimental scatter of the data is largest at this end of the plot. The experiments, however, clearly show that there is only a contribution of 5 to 10% of immobile protons (see also Fig. 1, curve C), and one can see that the immobile portion relaxes somewhat faster than the diffusing oil protons which may be seen in Fig. 2. For larger echo times, at $\Delta = 600$ ms the echo attenuation plot shows a smaller curvature for large attenuations than at the shorter time $\Delta = 100$ ms. How may this immobile fraction observed in the diffusion experiments be interpreted? At first we look at the transverse nuclear magnetic relaxation behaviour of the protons in the rape seeds. It is characterized by three components of the magnetization decay $M_\perp(t)$. A typical dependence of $M_\perp$ on time measured with the CPMG pulse sequence is shown in Fig. 8. The two slowly decaying components represent the contribution of oil protons with a transverse relaxation time T_2 of about 150 ms and about 50 ms. In Fig. 8, the magnetization decay of seeds with a moisture content of 12% shows a third component in the range of some ms which is assumed to represent water protons. Up to a water content of 6% there is no detectable water signal, and up to the highest water content of 40% T_2 only increases to about 5 ms. The reasons for this two-exponential behaviour may be the existence of two compartments of oil with different mobility.

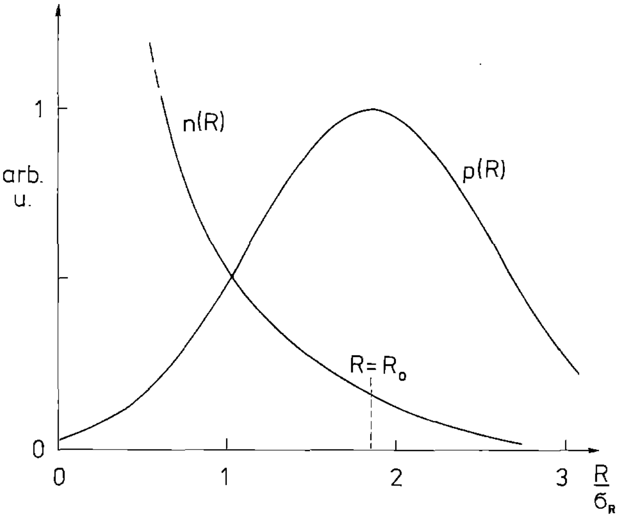

Fig. 7. Mass distribution $p(R)$ according to (14) (distribution (*ii*)) and number distribution $n(R)$ according to (22) of radius R. σ_R^2/R_0^2 was chosen to be 0.3

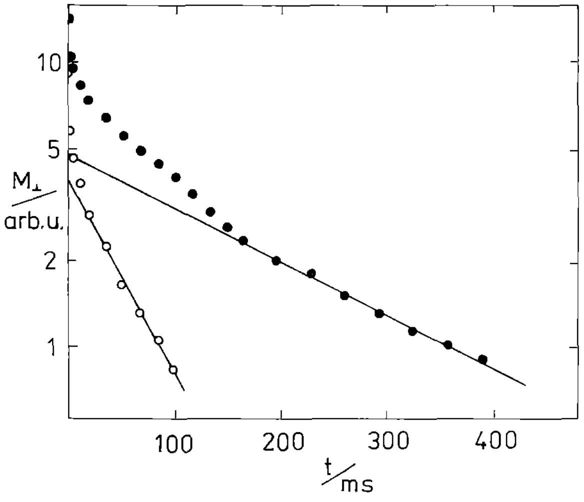

Fig. 8. Semilogarithmic plot of the transverse magnetization decay $M_\perp$ in rape seed (*Maras*) with moisture content of 12% measured with the CPMG pulse sequence. ●: experimentally determined $M_\perp(t)$; ○: difference between the most slowly decaying component of $M_\perp(t)$ (shown as straight line) and measured $M_\perp(t)$. At very short times a third component is seen; $T_2^l 210$ ms, $T_2^m = 65$ ms, $T_2^s = 2.5$ ms

To distinguish between the diffusional behaviour of these two oil components, a special experiment was performed. The stimulated echo sequence was not started with a $\pi/2$-rf-pulse but with the primary spin echo from a $\pi/2$-π-rf-pulse sequence applied before the stimulated echo sequence. In this way we are able to control the contribution of the faster and slower relaxing parts of the oil protons in the primary echo and hence in the echo attenuation by the variation of the time between the two rf-pulses of the primary echo experiment. This experiment has shown that the echo attenuation plot is not influenced

---

[1] With the distribution (*ii*) $n(R)$ diverges at $R \to 0$. In reality one has to cut the small left tail of the distribution (*ii*) at $R \leq 0$ or $R < 0.1$ or so

by the time between the first $\pi/2$-rf-pulse and the primary echo, it does not depend on the kind of oil protons prevailing in the signal. The two oil components seen in T_2-relaxation do not differ in the diffusional behaviour. We have to conclude that the non-single exponential T_2 behaviour of the oil protons arises from differences in the intramolecular mobility (between aliphatic and olefinic protons). This is also supported by the fact that the relaxation behaviour of the pure oil also show these two components. The overall mobility of the oil molecules must be uniform within the droplets. As a result of these investigations we have to connect the immobile fraction seen in the NMR-PFGT experiment not with oil protons but with a small portion of protons from another species which diffuse very slowly. They have, however, nuclear magnetic relaxation times which are not too small and are possibly the protons of lipids.

The self-diffusion coefficient of water in the rape seeds at the saturation content of water achieved in an atmosphere of 100% relative humidity after 4 days was measured to be $(4.2 \pm 0.8) \cdot 10^{-10}\ \mathrm{m^2\,s^{-1}}$, independent of the diffusion time Δ between 3 and 50 ms. The self-diffusion coefficient of bulk water is $2.3 \cdot 10^{-9}\ \mathrm{m^2\,s^{-1}}$ (Weingärtner 1982). In the rape seeds it is reduced to 20% of this value. This is typical for swollen polymer systems at these concentrations. From the sorption isotherms it follows that at $c \geq 6\%$ the water molecules tend to form clusters (Werner et al. 1990) which favours the fast diffusion at the high moisture content.

Conclusions

The self-diffusion of oil in rape seeds is found to be completely restricted for diffusion times $\Delta \geq 30$ ms. The oil diffuses within small droplets with impermeable surfaces. The echo attenuation plots show a distribution of droplet radii which may be mathematically well described by a Gaussian mass distribution of droplet radii. This implies a large number of very small droplets. Physically more realistic is a Gaussian number distribution of droplets with radius R and an immobile part of protons in the signal of the order of 5 to 10%. This model equally well describes the experimental results. From the experiment with variable spin echo times we have to conclude that in the droplets only one uniform diffusive mobility of the oil protons exists whereas the transverse magnetization decay shows two components. With the first distribution the mean radius of the droplets is about 0.7 µm, it somewhat depends on the variety of the rape seeds, and slightly decreases with increasing moisture content of the seeds. Since the droplet diameter is large in comparison to the size of the oil molecules, the hindrance of the mobility of the oil molecules by the droplet surface is small. The immobile part in the signal possibly arises from the lipid protons in the rape seeds. At a maximum water content of the seeds of 40%, the water self-diffusion coefficient is 20% of the bulk water self-diffusion coefficient. This value is typical for swollen polymer-solvent-systems at such high solvent concentrations.

Acknowledgements. The authors would like to thank J. Kärger and S. Limmer from the physics department of the Karl Marx University, Leipzig for valuable comments and discussions and O. Maev from the physics department of the Kazan State University who performed a great number of the measurements.

References

Callaghan PT (1984) Pulsed field gradient nuclear magnetic resonance as a probe of liquid state molecular organization. Aust J Phys 37: 359–387

Callaghan PT, Jolley KW, Lelievre J (1979) Diffusion of water in the endosperm tissue of wheat grains as studied by pulsed field gradient nuclear magnetic resonance. Biophys J 28:133–141

Callaghan PT, Jolley KW, Humphrey RS (1983) Diffusion of fat and water in cheese as studied by pulsed field gradient nuclear magnetic resonance. J Colloid Interface Sci 93: 521–529

Fleischer G, Geschke D, Kärger J, Heink W (1985) Peculiarities of self-diffusion studies with polymer systems by the NMR pulsed field gradient technique. J Magn Res 65: 429–443

Kärger J, Pfeifer H, Heink W (1988) Principles and application of self-diffusion measurements by nuclear magnetic resonance. Adv Magn Res 12: 1–89

Maklakov AI, Skirda VD, Fatkullin NF (1987) Self-diffusion in polymer solutions and melts (in russian). Isd Kazanskovo universiteta, Kazan USSR

Stilbs P (1987) Fourier transform pulsed-gradient spin-echo studies of molecular diffusion. Progr NMR Spectr 19: 1–45

Tanner JE (1978) Transient diffusion in a system partitioned by permeable barriers. Application to NMR measurements with a pulsed field gradient. J Chem Phys 69: 1748–1754

Tanner JE, Stejskal EO (1968) Restricted self-diffusion of protons in colloidal systems by the pulsed gradient spin echo method. J Chem Phys 49: 1768–1777

Von Meerwall ED (1983) Self-diffusion in polymer systems, measured with field gradient spin echo NMR methods. Adv Polymer Sci 54: 1–29

Von Meerwall ED, Ferguson RD (1981) Interpreting pulsed-gradient spin-echo diffusion experiments with permeable membranes. J Chem Phys 74: 6956–6963

Weingärtner W (1982) Self-diffusion in liquid water. A reassessment. Z Phys Chem NF 132: 129–149

Werner A, Fleischer G (1990) Study of water and oil diffusion in rape seeds with sorption/desorption and NMR techniques. (in preparation)