Determination of Emulsion Size Distribution by NMR Restricted Diffusion Measurement

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During the early stage of our study on dispersed-phase texture in porous media, we tested the technique proposed by Packer and Rees (1972) that uses NMR (nuclear magnetic resonance) restricted diffusion measurement to determine bulk emulsion-size distribution.

It has been known for some time (Hahn, 1950; Carr and Purcell, 1954) that self-diffusion of molecules having nuclear magnetic moments can be detected by pulsed NMR in the presence of various magnetic field gradients. The method of using pulsed magnetic field gradients was described first by Stejskal and Tanner (1965). A spin echo pulse sequence with two gradient pulses is shown in Figure 1. The final echo intensity reflects the effect of diffusion occurring during the time interval Δ between the two gradient pulses. The NMR attenuation is defined as the ratio of the echo intensities with and without the presence of external field gradients:

$$R=\frac{I_{\text{with gradient}}}{I_{\text{without gradient}}}$$

The NMR attenuation, as defined above, eliminates the effects of finite relaxation times and therefore contains only the effect of diffusion. In bulk liquid, where molecules can diffuse randomly in sufficiently large space, the NMR attenuation R is related to other parameters by (Stejskal and Tanner, 1965; Tanner, 1969):

$$\ln R=-\gamma^2 g^2\delta^2\left(\Delta-\frac{1}{3}\delta\right)D \tag{1}$$

Thus, the diffusion coefficient D of the liquid in question can be simply determined from the slope of the linear relation between measured values of $\ln R$ and the diffusion time Δ. In dispersed systems, where the diffusion of molecules in the dispersed elements is restricted by the phase boundaries, however, such a simple relation is not applicable. The attenuation R will in general depend not only on g, Δ, δ, and D, but also on the geometry of the dispersed phase. For example, the NMR attenuation due to the diffusion of protons in a sphere with diameter $2a$ can be calculated as (Murday and Cotts, 1968):

$$R(\Delta,\delta,a)=\exp\left[-2\gamma^2 g^2\sum_{m=1}^{\infty}\frac{1}{\alpha_m^2(\alpha_m^2a^2-2)}\left\{\frac{2\delta}{\alpha_m^2 D}-\frac{2+e^{-\alpha_m^2D(\Delta-\delta)}-2e^{-\alpha_m^2D\Delta}-2e^{\alpha_m^2D\delta}+e^{-\alpha_m^2D(\Delta+\delta)}}{(\alpha_m^2D)^2}\right\}\right] \tag{2}$$

where α_m is the mth positive root of the Bessel function equation

$$\frac{1}{\alpha a}J_{3/2}(\alpha a)=J_{5/2}(\alpha a).$$

Equation 2 relates the NMR attenuation with the size of the dispersed phase, a. This important fact suggests that information about the dispersed-phase size distribution can be obtained from NMR-restricted diffusion measurements.

Several research groups have used NMR-restricted diffusion measurement to determine size distribution of emulsion droplets (Packer and Rees, 1972; Callaghan et al., 1983; Van Den Enden et al., 1990). The measurement can be made by either varying the field gradient g or the diffusion time Δ. In our experiment, we adopted the approach by Packer and Rees, which measures the NMR attenuation as functions of diffusion time Δ.

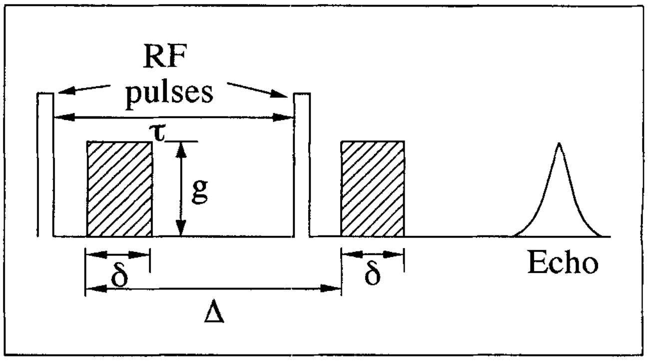

Figure 1. Pulse sequence diagram of a spin echo with pulsed magnetic field gradient.

The dispersed-phase elements in bulk emulsions are spherical in shape. The experimentally observed NMR attenuation $<R(\Delta, \sigma)>$ can be expressed in terms of the calculated attenuation of individual droplets R (Eq. 2) through the relation (Packer and Rees, 1972):

$$<R(\Delta, \delta)> = \frac{\int_0^\infty a^3 P(a) R(\Delta, \delta, a) da}{\int_0^\infty a^3 P(a) da} \tag{3}$$

where $P(a)$ is the droplet-size distribution, and the factor a^3 reflects the fact that the NMR intensity is proportional to the number of protons. The functional form of $P(a)$ is not unique. Packer and Rees adopted a log-normal function:

$$P(a) = \frac{1}{2a\sigma(2\pi)^{1/2}} \exp\left[-\frac{(\ln 2a - \ln \xi)^2}{2\sigma^2} \right] \tag{4}$$

By fitting their experimental data with Eq. 3, Packer and Rees were able to determine the parameters ξ and σ in Eq. 4 and hence obtain the size distribution of the water droplets in their water-in-oil emulsion samples. However, they did not give independent quantitative verification of the distribution functions obtained by the NMR method, and their measurement of oil-in-water samples were not successful.

In this work, we extended the methods of Packer and Rees to oil-in-D_2O emulsions, and attempted to verify the droplet-size distribution by an independent method. In the discussion below, we will also address the importance of the relation between the diffusion coefficient and the average droplet size for the restricted diffusion measurements and explain its effects on the previously unsuccessful measurement of oil-in-water samples.

Experiment

All samples studied in this experiment were oil-in-D_2O emulsions. D_2O and H_2O have very similar chemical properties. D_2O was used because the NMR resonance frequency of deuterons is quite different from that of protons in oil; therefore, we can select the experimental parameters so that only NMR signals from oil molecules are seen. All samples were prepared as follows: 2 g of oil (*n*-hexadecane or *n*-octane) was added to a surfactant solution consisting of 0.2 g of alpha olefin sulfonate (AOS) and 0.5 g of D_2O; the solution was then stirred by a thick edged propeller at a fixed speed for a fixed amount of time. The oil droplet sizes could be roughly controlled by changing the stirring speed and duration. The final emulsion samples contained many droplets visible to the naked eye. These samples were stable for several weeks without dramatic changes.

NMR measurements were performed on a GE MRI imager. The superconducting magnet provides a 2-Tesla magnetic field corresponding to a proton resonant frequency of about 85.55 MHz. The pulsed field gradient coil can deliver a field gradient up to 20 Gauss/cm.

Self-diffusion coefficients, D, of the oils were obtained by measuring NMR restricted diffusion on bulk oil samples, as described earlier (Eq. 1). The proton spin-lattice relaxation times T_1 of emulsion samples was measured using the inversion recovery method. The experimental values of D and T_1 of both oils are listed in Table 1. Proton T_2 values of emulsion samples were also estimated using the Hahn spin echo sequence. All observed T_2 values were less than 200 ms. The relatively short T_2 limits the maximum diffusion time $\Delta_{\max}$ if the spin echo method is used. This problem can be overcome by using the stimulated echo method, which takes advantage of the relatively long T_1. In our experiments, spin echo was used for short Δ's (< 150 ms), where stimulated echo did not give good measurements due to the overlapping of several different echoes. Stimulated echoes were used for longer Δ where the spin echo signals became too small to be observed.

Table 1. Diffusion Coefficients of Pure Oils and Spin-Lattice Relaxation Times of the Oil-in-D_2O Emulsion Samples at Room Temperature

	n-Hexadecane	*n*-Octane
D (cm^2/s) (Bulk Oil)	3.74×10^{-6}	2.33×10^{-5}
D (cm^2/s) (Literature Value)	3.92×10^{-6}*	2.00×10^{-5}**
T_1 (s) (Emulsion)	0.68	2.05

* From Ertl and Dullien (1973).
** From Douglass and McCall (1958).

NMR attenuation was measured as functions of both the diffusion time Δ and the gradient pulse width δ. A nonlinear least squares algorithm was used to fit Eq. 3 to the experimental data and obtain the parameters ξ and σ in Eq. 4.

To obtain an independent emulsion-size distribution measurement, the droplet sizes were also measured using an optical imaging system, consisting of a microscope, a video camera, a personal computer, and an image analysis software. During the measurement, the emulsion sample was placed on a glass plate and covered by a thin, light-weight glass slide. A near single layer of emulsion was generated between the two glass slides. Most of the emulsion droplets were able to flow between the two slides, while some very large droplets remained at the same place as the slides were tilted. This indicated that the thin glass cover was supported by these very large droplets, and the size of the smaller droplets were not greatly distorted. The two-dimensional microscope image of the emulsion sample was captured by the camera and stored in the computer. The image analysis software then counted the droplets and measured their sizes. The data were analyzed to obtain the size distribution. This procedure gave a fairly good count of the medium-sized droplets; nevertheless, it could miscount those extremely small droplets ($a < 1$ μm), which were obscured by larger ones. These tiny droplets, however, did not contribute greatly to the NMR measurement, because their NMR intensities were negligible compared with those from the larger droplets. Furthermore, the diffusion in these droplets became saturated much faster than in larger droplets (see the discussion below) so they did not contribute significantly to the change of NMR attenuation. Thus, miscounting of these tiny droplets would not affect the comparison between the size distributions obtained by the optical method and that by the NMR method.

Results and Discussion

Two measured NMR attenuations for a *n*-octane sample with different gradient field pulse width are presented in Figure 2

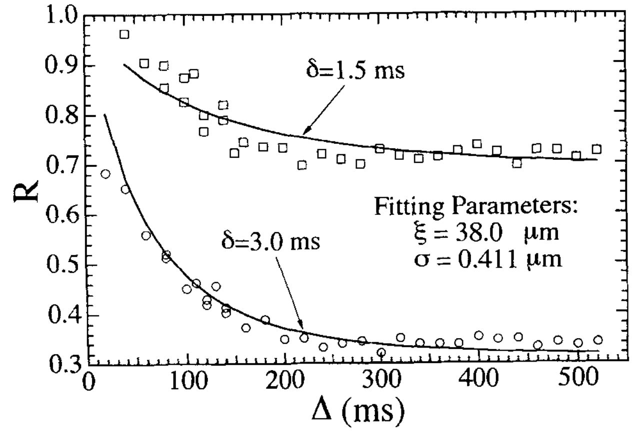

Figure 2. NMR attenuation of a *n*-octane in D_2O emulsion sample.

as functions of the diffusion time, Δ. The data were taken under a field gradient $g = 10$ Gauss/cm with pulse width $\delta = 1.5$ ms and $\delta = 3.0$ ms, respectively. The solid curves in Figure 2 are the calculated attenuation using Eqs. 3 and 4 with $\xi = 38.0$ μm and $\sigma = 0.411$ μm. The corresponding droplet-size distribution function is plotted in Figure 3 as the solid curve.

The size distribution function obtained by the optical method is also plotted in Figure 3 as the dashed line. It has very similar features as the one measured by the NMR method. Despite its shortcoming discussed in the previous section, the optical method gave a quantitative verification of the NMR restricted diffusion method.

Among the emulsion samples made with *n*-hexadecane and *n*-octane, we were only able to observe a strong restricted diffusion effect on the *n*-octane samples. The data from the *n*-hexadecane samples failed to give stable converged distribution parameters, ξ and σ, during the nonlinear fitting. Such different behaviors were caused by the very different diffusion coefficients of the two oils. To understand this phenomenon better, we prepared Figure 4, which displays the NMR attenuation during an ideal restricted diffusion process.

We can define a characteristic time for a given emulsion sample, $\tau_c = a_m^2/D$, which is the time for an oil molecule to diffuse across an oil droplet of radius a_m, with a_m being the average radius of all droplets in the emulsion. A complete observed restricted diffusion process can be divided into three regions (Figure 4). In region I, where the diffusion time $\Delta \ll \tau_c$, the measured NMR signals are mostly due to the bulk diffusion in large droplets, and the dependence of ln*R* is nearly linear to Δ. When diffusion time becomes longer and comparable with τ_c, more and more oil molecules hit the droplet boundaries, and their diffusion become restricted. As a result, the dependence of ln*R* on Δ becomes nonlinear (region II). In region III, where $\Delta \gg \tau_c$, most molecules in the droplet have impacted on the boundary, and memory of the initial diffusion is lost.

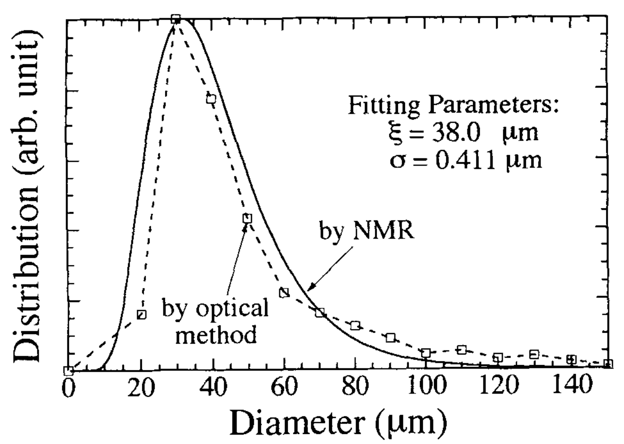

Figure 3. Size distribution function of the *n*-octane emulsion sample.

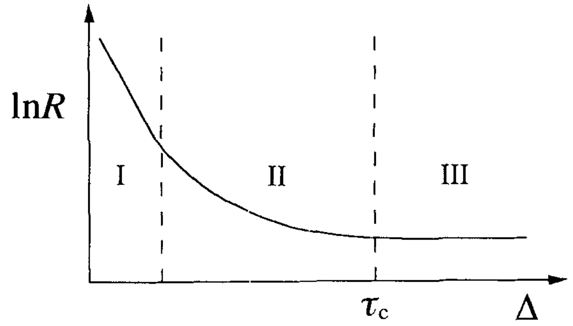

Figure 4. NMR attenuation of an ideal restricted diffusion process.

In this case, the observed attenuation becomes independent of Δ. To obtain stable distribution parameters, ξ and σ, from the fitting algorithm describe above, the NMR attenuation data must: 1) be complete, which should include all three regions in Figure 4 and thus requires the maximum diffusion time Δ_{max} be larger than τ_c; 2) have reasonable resolution in all the regions. In our experiment, the maximum diffusion time Δ_{max} is limited by the spin-lattice relaxation time T_1 of the emulsion samples, $\Delta_{max} \sim T_1$. If Δ is much larger than T_1, the NMR signal will be too weak to observe even by the stimulated echo method. Hence, for a given oil with a certain diffusion coefficient *D*, the average emulsion droplet size must be small enough for $\Delta_{max} > \tau_c$. The features of the observed NMR attenuation of our *n*-hexadecane emulsion make us believe that this caused the unsuccessful determination of the distribution parameters for such samples. On the other hand, reasonable resolution of NMR attenuation cannot be obtained in all regions if, for example, $\tau_c \ll T_1$, which causes all three regions to collapse in the short period of time. This will happen if the droplet sizes are too small. In this case, the fitting algorithm used here will not give good distribution parameters. This might be part of the reason that Packer and Rees failed on their oil-in-water emulsion samples. It is possible, however, to obtain droplet-size distribution in region III using other methods (Van Den Enden et al., 1990; Callaghan et al., 1983).

Conclusions

The current study extended the work by Packer and Rees and further provided a quantitative verfication to the validity of using NMR-restricted diffusion measurement to determine bulk emulsion-size distributions.

The bulk emulsion droplet-size distribution obtained from NMR-restricted diffusion measurements quantitatively reflects the real droplet-size distribution. The effectiveness of this method depends on the average droplet size and the magnitude of the dispersed-phase diffusion coefficient, D. The effects of the relation between D and the size of the dispersed phase need to be considered when applying this method to other dispersed phases.

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Notation

a = spherical droplet radius
a_m = typical spherical droplet radius
D = diffusion coefficient
g = magnetic field gradient intensity
R = NMR attenuation
$<R>$ = average NMR attenuation

Greek letters

δ = magnetic field gradient pulse width
Δ = diffusion time
Δ_{max} = maximum diffusion time
τ = echo time
γ = gyromagnetic ratio
ξ = average droplet size
σ = standard deviation of size distribution

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