

A New Strategy for Evaluating the Self-Diffusion Coefficient in Restricted Diffusion: Case of Polydisperse Emulsions with Small Mean Radii[†]

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In emulsion systems one of the key points is to directly obtain information on both mobility and polydispersity from the experimental data. Recently we proposed a polynomial method to obtain the dispersed phase self-diffusion coefficient from experimental data lying on the left of a limiting value of δ (the characteristic magnetic field gradient pulse time in a PGSE-NMR experiment). However, if the mean radius of the droplet is small, all of the experimental points are located on the right of this limiting value, and a new computational strategy is proposed to achieve the self-diffusion coefficient and the distribution function at the same time. PGSE-NMR results and optical microscopy literature data are compared to test the method.

Introduction

The study of the self-diffusion of pure liquids or solutions is of great technical and scientific interest. From the latter point of view it has become especially important to understand the liquid state.¹ No less important is the study of the molecular motion in colloidal dispersions, where it can provide information on the dispersed phase structure.²

The molecular mobilities are conveniently characterized by the self-diffusion coefficient D . The knowledge of this coefficient and its dependence on physical properties, such as concentration, temperature, pressure, and so on, is a powerful tool to investigate the structure of both homogeneous and heterogeneous systems.^{3,4} The NMR spin-echo technique for measuring self-diffusion, originally suggested by Hahn,⁵ has many advantages over conventional tracer techniques. Experiments are less time-consuming, small volumes of sample are needed so that the control of temperature and pressure is straightforward, and finally there is no need to set up and maintain a concentration gradient.

For homogeneous systems, the self-diffusion coefficient and the maximum echo intensity attenuation are linked by a simple mathematical relationship, so that D can be easily extracted from the experimental data. For heterogeneous systems, and particularly for emulsions, the experimental evidence of restricted diffusion is widely assessed.⁶ In this case the experimental data are linked to D through complicated equations so that getting the desired self-diffusion coefficient is less straightforward.

Murday and Cotts, in their study on liquid lithium,⁷ indicated an iterative procedure to evaluate D in systems undergoing restricted diffusion in spherical cavities. Their method, however, can be applied only to monodisperse systems where the size of

the spherical cavity is known. On the contrary, real emulsions exhibit a more or less large polydispersity and in general even their mean size is unknown.

In recent years, we have studied via NMR the restricted diffusion phenomenon in the presence of polydisperse emulsions.^{8–10} We showed that it is possible to evaluate the distribution function, directly from experimental data, without any a priori hypothesis about the distribution form. The method, called direct method, gives reliable results provided that the self-diffusion coefficient is known.

For a water in oil (w/o) emulsion system such parameter is generally only estimated. Recently, a new approach to calculate the self-diffusion coefficient in such system has been proposed by us.¹⁰ Such a method is based on the opportunity to have, in a plot of the echo attenuation vs the pulsed gradient duration δ , experimental data lying on the left of a limiting (boundary) value δ_b (see next section for details). A polynomial fit of the experimental data allowed us to obtain the self-diffusion coefficient, D , and the second and fourth moments, μ_2 and μ_4 , of the distribution. However, if the mean radius of the droplet in the emulsion is small (compared to $\sqrt{D\delta}$) the experimental points are all located to the right of the value δ_b , and therefore the polynomial fitting cannot be used for determining the coefficient D .

The purpose of the present paper is to show how the self-diffusion coefficient can be calculated directly from experimental data also in these complex cases.

Theory

Basic Equation. In heterogeneous systems the self-diffusion coefficient appears to depend on the time scale of the experiment. At very short times a spread in the self-diffusion coefficients can be observed, as a consequence of local changes in viscosity. At long observation times (peculiar to spin-echo NMR experiments) a uniform averaged diffusion coefficient is observed, since the molecules have the opportunity to repeatedly

[†] This paper is dedicated to the memory of Professor Americo Inglese (1946–1998).

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sample all of the different environments. One particular kind of system frequently met in emulsions consists of droplets (spherical barriers) in an otherwise homogeneous medium (continuous phase). If the diffusion of molecules randomly moving inside a droplet is observed over a short enough time, so that only very few molecules experience the effect of the barriers, the observed motion is characteristic of the bulk alone: free diffusion. When the time of observation increases, many more molecules are reflected by barriers so that their global displacement is lower than would have been if no barriers at all were present: restricted diffusion.

Obviously, to experimentally investigate the molecular motion it is necessary to sample the system at different moments. For this purpose pulsed gradient spin-echo (PGSE)-NMR is a suitable technique, allowing the observation of molecular displacements from below 100 nm up to several microns.

A rigorous treatment of the echo attenuation in the case of free diffusion gives the following dependence of the signal on the applied gradient¹

$$E(\Delta, \delta, R, g) = E_0 \exp(-\Delta/T_2) \exp[-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)] \quad (1)$$

with γ being the magnetogyric ratio, and, to avoid complications due to spin-spin relaxation time (T_2), it is convenient to measure $E(\Delta, \delta, R, g)$ as a function of δ for fixed value of the observation time (Δ) and the field gradient strength (g). This procedure allows not to take into account the $\exp(-\Delta/T_2)$ factor in eq 1, leading to an easy calculation of the self-diffusion coefficient.

This procedure applies to nuclear spins undergoing a three-dimensional random walk, described by diffusion equation. On the contrary, molecules randomly moving inside a spherical cavity (droplet) are free to diffuse until they reach the boundary. If the molecules cannot leave the cavity they will be reflected (by the barrier) back to the core of the droplet. The translational diffusion of such molecules will be therefore restricted and eq 1 will not be valid anymore. In this last case the expression of the echo attenuation and its dependence on Δ , δ , g , and R is⁷

$$E(q, R) = \exp\left(-\frac{2\gamma^2 g^2}{D} \sum_{m=1}^{\infty} \frac{1}{\alpha_m^4 (\lambda_m^2 - 2)} f_m(q, R)\right) \quad (2)$$

where $q = \gamma\delta g/2\pi$ and

$$f_m(q, R) = \frac{2\delta - \frac{2 + e^{-\alpha_m^2 D(\Delta - \delta)} - 2e^{-\alpha_m^2 D\Delta} - 2e^{-\alpha_m^2 D\Delta} + e^{-\alpha_m^2 D(\Delta + \delta)}}{\alpha_m^2 D} \quad (3)$$

where $\lambda_m = \alpha_m R$ is the m th the root of equation

$$(1/2)J_{3/2}(\lambda) - \lambda J'_{3/2}(\lambda) = 0 \quad (4)$$

where $J_{n/2}(\vartheta)$ is the Bessel coefficient¹² of a generic argument ϑ and order $n/2$ and D the self-diffusion coefficient of the dispersed liquid inside the droplet. It has to be pointed that in eq 2, T_2 is assumed to be independent of R . Equation 2 describes the restricted diffusion occurring in an isolated sphere. Due to its mathematical complexity, without any a priori information on the droplet size, it is hopeless to evaluate confidently the self-diffusion coefficient.

Since the droplet size is 4 orders of magnitude larger than the dispersed phase molecules, we can consider the sphere spatially fixed, i.e., the droplet translational motion is negligible (furthermore, in most emulsions of practical interest the continu-

ous phase is highly viscous). Equation 2 will describe the diffusion occurring within the droplets, even in the case of polydisperse systems. Assuming a spherical geometry for the dispersed phase, the ^1H NMR experiment will provide information on proton spin density in the sphere, that is on the volume of the sphere. The observed echo attenuation (I) can thus be written in terms of a generic droplet volume fraction distribution $\Phi(R)$:

$$I = \int_0^L E(q, R) \Phi(R) dR \quad (5)$$

where $E(q, R)$ is defined by eq 2 and $\Phi(R)dR$ is

$$\Phi(R)dR = \frac{R^3 P(R) dR}{\int_0^L R^3 P(R) dR} \quad (6)$$

where $P(R)dR$ is the fraction of droplets with radius lying between R and $R + dR$ and $L = \sqrt{2D\Delta}$ replacing the ∞ term as the upper limit of the integration in eq 5 for the reasons reported in ref 9. Previously we reexamined the nature of the restricted diffusion occurring in polydisperse systems, finding that when $\Phi(R)$ is within the limit of the diffusion length L (i.e., $L = \sqrt{2D\Delta}$), the experimental data contain enough information to describe the distribution function in any detail.⁸ We also showed that when the dimensionless quantities $z = R/L$ and $x = \delta/\delta_{\max}$ (where δ_{\max} is the largest value experimentally used for the gradient pulse duration) are utilized, eq 5 can be transformed in a Fredholm integral equation of the first kind⁹

$$I(x) = \int_0^1 E(x, z) \Psi(z) dz \quad (7)$$

We proposed two methods to evaluate the dimensionless volume fraction distribution $\Psi(z)$ directly from experimental data. Both methods are flexible and robust, so that it is quite easy to obtain from the experimental data the $\Psi(z)$.⁹

Once $\Psi(z)$ is known, to evaluate $\Phi(R)$ it is necessary to know L , therefore D . In the case of w/o emulsions, this D value can be approximated to that of aqueous solutions, although in many emulsions of applicative interest such an assumption is questionable.¹⁰ For o/w emulsions, due to the lack of extensive literature data and to the enormous variability of oil phases usually met in real-life emulsions, the situation is much more delicate and it is often impossible to safely estimate the self-diffusion coefficient inside the droplets (see Conclusions in ref 10).

A possible way to overcome this kind of problems is to find a way to solve eq 2 to extract the unknown D .

Polynomial Methods. Since exact analytical calculation of D from eq 2 or eq 5 is hopelessly difficult, an attempt to evaluate D by series expansions of eq 2 has been made.

Using the dimensionless parameter $\theta = (D\delta/R^2)$ the following relations were built:¹⁰

$$f(\delta) = \frac{1 - I(q)}{\delta^2} = \gamma^2 g^2 \frac{\mu_2}{5} - \frac{1}{3} D \gamma^2 g^2 \delta + \dots \text{ for } \theta < 1 \quad (8)$$

and

$$g(\delta) = 1 - I(q, R) = -\frac{166}{7875} \frac{\gamma^2 g^2}{D^2} \mu_6 + \frac{16}{175} \frac{\gamma^2 g^2}{D} \mu_4 \delta + \dots \text{ for } \theta > 1 \quad (9)$$

where μ_k is the k th moment of the distribution function.

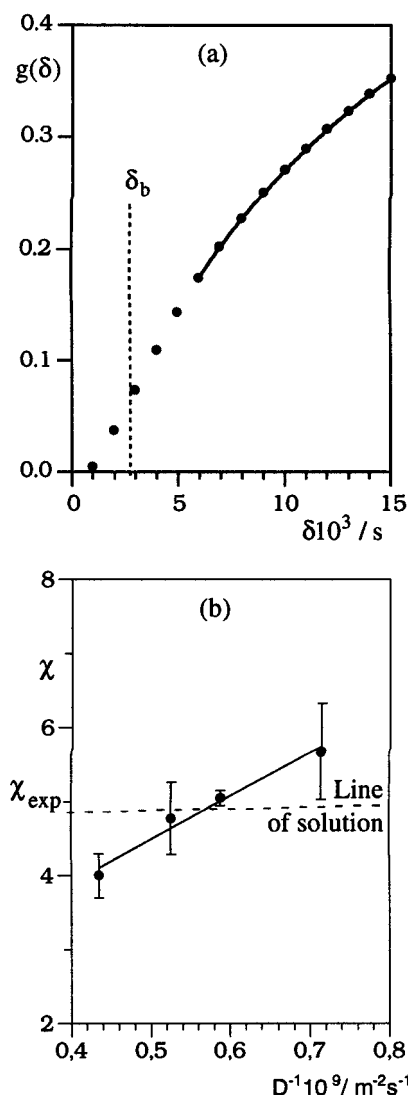


Figure 1. Results of a simulated PGSE-NMR experiment: (a) $g(\delta) = 1 - I(q, R)$ vs δ (see eq 9); solid line represents polynomial fit to eq 9 to obtain χ_{exp} ; dashed line indicates the boundary value δ_b . (b) χ -points obtained applying the direct method for different D values. The intersection point between this line and χ_{exp} (line of solution) gives the unknown self-diffusion coefficient.

Using an approximated initial estimate of D , it is possible to obtain a separation value, δ_b , which divides the experimental interval into two subintervals. On the left subinterval, one computes the coefficients of eq 8, while on the right subinterval those of eq 9, in both case by means of polynomial least-squares fits (a detailed description of this procedure is given elsewhere¹⁰).

It is important to note that, besides the D coefficient, in this way the only accessible information about the distribution function are the moments μ_2 , μ_4 , or μ_6 . There is, however, an alternative way to extract the distribution form from the experimental data. We can use the calculated (via eq 8) coefficient D for solving the integral eq 7 by means of the direct method. Now, the coefficients μ_2 and μ_4 calculated by means of eq 8 and eq 9 can be used to check the results. In other words, the combination of the direct and polynomials method is an effective tool to investigate polydisperse emulsions.

However, if the mean dimensions of the droplets are small, the value δ_b is so small that all (or almost all) of the experimental points lie in the region $\delta > \delta_b$. In this case only

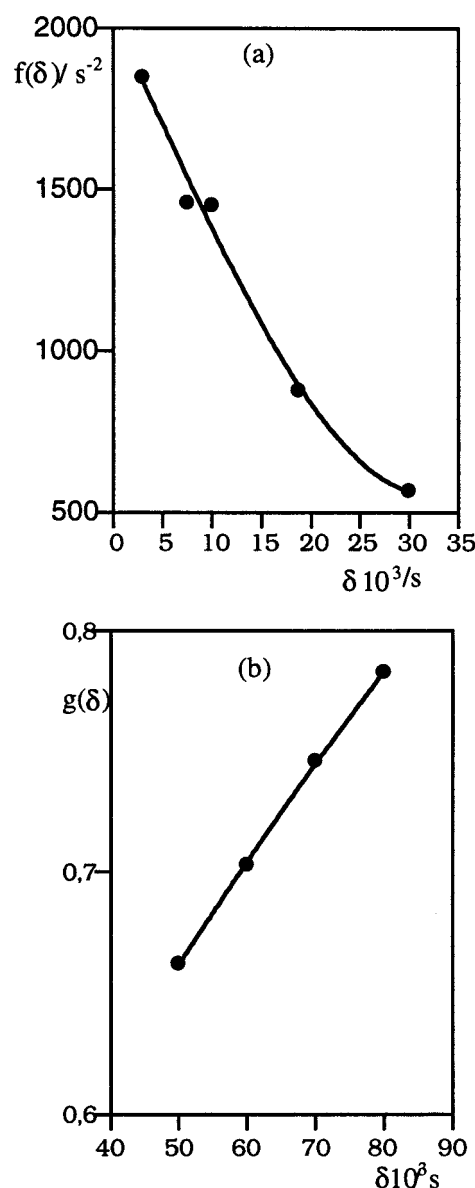


Figure 2. Benzene (48.5 wt %), water (48.5 wt %), Triton X-100 (3 wt %) emulsion at 25 °C. (a) $f(\delta) = 1 - I(q, R)/(\delta)^2$ vs δ (see eq 8); solid line is the polynomial fitting to experimental data in the subinterval $\delta < \delta_b$. (b) $g(\delta) = 1 - I(q, R)$ vs δ (see eq 9); solid line is the polynomial fitting to experimental data in the subinterval $\delta > \delta_b$.

eq 9 may be fitted to a polynomial. Since the distribution is unknown it follows that in this case the determination of D is not feasible.

Results and Discussion

To illustrate this last case, the simulation of a PGSE-NMR measurement pertaining to a w/o emulsion is presented in Figure 1a. The simulation is based on a procedure already described.¹⁰ Basically, the polydispersity is simulated by means of a log-normal distribution whose parameters are $R_0 = 2.5 \times 10^{-6}$ m and $\sigma = 0.4$ while the experimental conditions are $\Delta = 0.050$ s, $g = 0.3$ Tm⁻¹, and $D = 1.70 \times 10^{-6}$ m² s⁻¹. Through the relationship $D\delta_b = R^2$ it is possible to evaluate δ_b since R^2 can be estimated by the slope of the first experimental points¹⁰ (simulated in this instance) and the D value is assumed to be that of pure water at the same temperature. By means of these assumptions, $\delta_b = 0.0026$ s and such a threshold value is indicated in Figure 1a by a vertical line, where it is evident

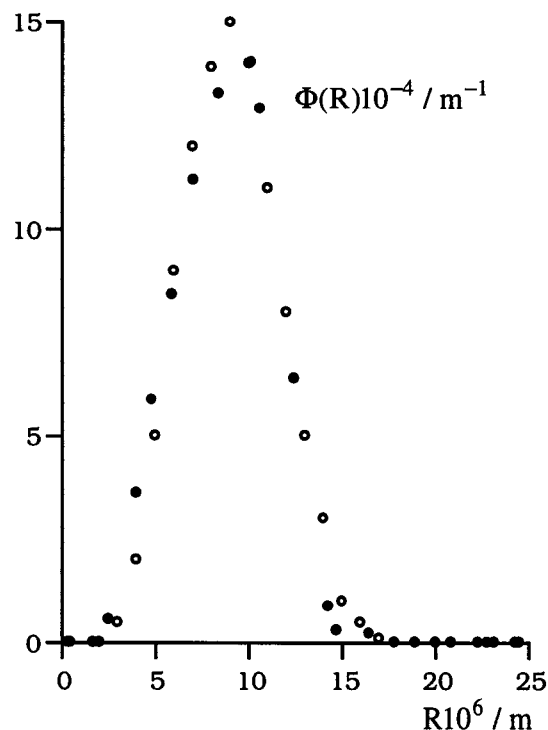


Figure 3. Benzene (48.5 wt %), water (48.5 wt %), Triton X-100 (3 wt %) emulsion at 25 °C. Comparison of the volume fraction distribution calculated from the PGSE-NMR data by means of the direct method (●) with that measured by means of optical microscopy (○).

that all (or almost all) of the data points are in the region $\delta > \delta_b$. Therefore only eq 9 can be applied to these data.

Since eq 9 depends only on the quantities μ_{4+2n}/D^{2n} , it follows that it is impossible to extract separately D and μ_{2n} from the experimental data. Furthermore, in the case of mean radii sufficiently small, modifying the experimental conditions is practically impossible. It follows that it is necessary to change the computational strategy. Obviously, if the coefficient D were known, it would be possible by means of polynomial fitting to calculate the fourth moment and vice versa. For the particular case under consideration, we find that the best fit to experimental data is obtained using a polynomial of fifth degree (see Figure 1a). Furthermore, assuming $D = 1.70 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, it results that $\mu_4 = (3.0 \pm 0.6) \times 10^{-22} \text{ m}^4$. When the calculated μ_4 moment is compared to the true one, $\mu_4^{\text{true}} = 2.9 \times 10^{-22} \text{ m}^4$, the extremely good agreement between the two leads us to conclude that as long as D is known, μ_4 can be accurately calculated. Such a conclusion leads to an important consideration: if μ_4 can be calculated in an independent way, the polynomial least-squares procedure can be used to obtain the D value.

New Computational Method. Let χ be the coefficient of the linear term of eq 9, that is

$$\chi = \frac{16}{175} \frac{\gamma^2 g^2}{D} \mu_4 \quad (10)$$

Let solve eq 7 by means of the direct method in order to build the distribution function, allowing D to assume a spread of values $D^{(1)}, D^{(2)}, D^{(3)}, \dots, D^{(n)}$. Let $\mu_4^{(1)}, \mu_4^{(2)}, \mu_4^{(3)}, \dots, \mu_4^{(n)}$ denote the corresponding fourth moments of the distribution to be used in order to calculate the quantity $\chi^{(n)}$ for each value of n , and χ_{exp} the coefficient obtained by polynomial fitting of the experimental data. The evaluation of the unknown D is now possible by plotting $\chi^{(n)}$ vs $D^{(n)}$ and the χ_{exp} value in the same

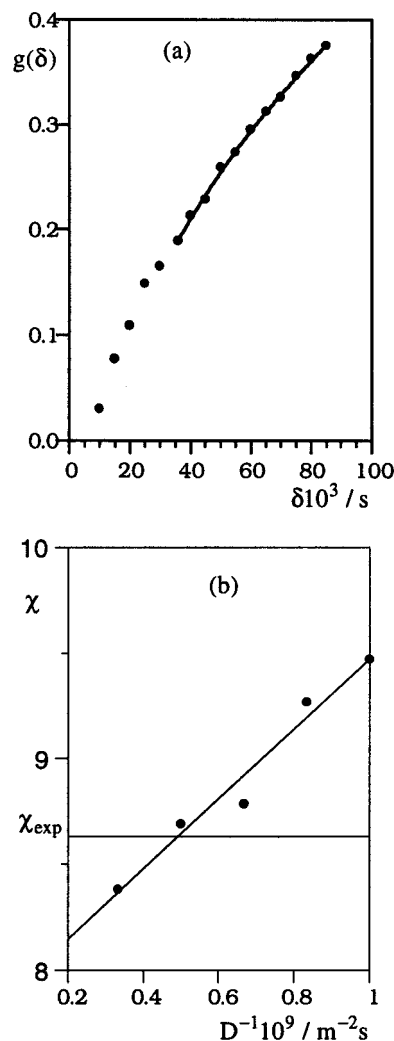


Figure 4. Xylene (48.5 wt %), water (48.5 wt %), Triton X-100 (3 wt %) emulsion at 25 °C. (a) $g(\delta) = 1 - I(q, R)$ vs δ (see eq 9); solid line represents polynomial fit to eq 9 to obtain χ_{exp} ; (b) χ -points obtained applying the direct method for different D values. The intersection point between this line and χ_{exp} gives the unknown self-diffusion coefficient.

graph (line of solution of Figure 1b). The intersection of the two curves locates the points which simultaneously satisfy both the experimental curve and the distribution function. In this way it is possible to unambiguously determine the unknown D value. When the evaluation of $\chi^{(n)}$ can be carried out keeping Δ constant, $\chi^{(n)}$ results a linear function of D^{-1} and the use of the graphical method is straightforward. Applying this procedure to the data presented in Figure 1b, one obtains a D value of $1.75 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ which differs from the true one by less than 3%.

Test on Experimental Data and Comparison with Microscope Photographs. To check the reliability of the proposed method, a test on its ability to evaluate the coefficient D and the capacity to reproduce the distribution function must be performed. This was achieved verifying the agreement between the results obtained with our method with those reported in ref 13. In that paper three different o/w emulsions were investigated. The emulsions were made with 3 wt % Triton X-100, 48.5% of water, and 48.5% of either benzene, toluene, or xylene, which were studied with PGSE-NMR and, at least for two of them (benzene and xylene), with optical microscopy. The authors did not use PGSE results to draw out the distribution. On the contrary, the radii extract from the microscope photographs (averaged with the volume fraction distribution) were used to

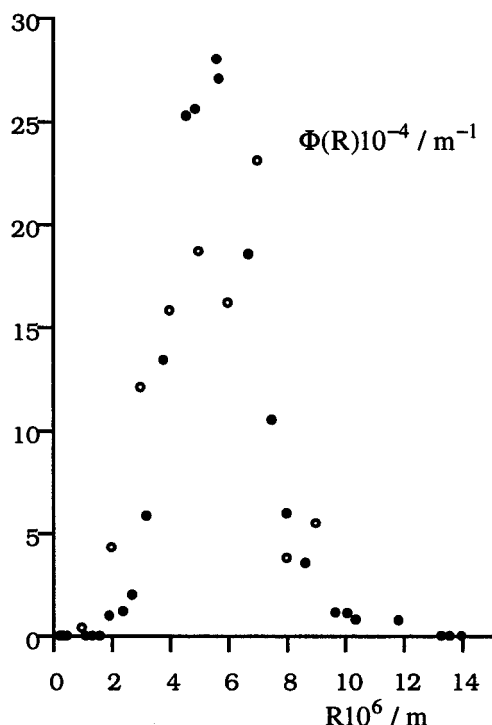


Figure 5. Xylene (48.5 wt %), water (48.5 wt %), Triton X-100 (3 wt %) emulsion at 25 °C. Comparison of the volume fraction distribution calculated from the PGSE-NMR data by means of the direct method (●) with that measured by means of optical microscopy (○).

verify the consistency of eq 2 with experimental data. To do this, they made an assumption for the self-diffusion coefficient of the pure oil. Such an assumption was verified a posteriori by means of relaxation time measurements. On the contrary, in the present paper we will directly estimate both D and $\Phi(R)$ from the echo decay, and the optical microscopy data will be used only to check our results.

Regarding the benzene emulsion, the optical microscopy data give (for the volume fraction distribution) $\mu_2 = 8.9 \times 10^{-11} \text{ m}^2$, $\mu_4 = 1.02 \times 10^{-21} \text{ m}^4$ and $\mu_6 = 1.4 \times 10^{-31} \text{ m}^6$.

From the initial slope of the PGSE-NMR data, we obtain $\delta_b = 0.0034 \text{ s}$, thus there are experimental points both in the interval $\delta < \delta_b$ and in $\delta > \delta_b$ (Figure 5 in ref 13). It follows that both eqs 8 and 9 can be applied to this emulsion.

In the left δ interval, the best equation fitting the experimental data is a polynomial of second degree (see Figure 2a), whose coefficients give $D = (2.2 \pm 0.3) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $\mu_2 = (9.1 \pm 0.3) \times 10^{-11} \text{ m}^2$. The calculated D value is in good agreement with that measured by Mills¹⁴ for pure benzene, $D = 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The μ_2 value is also in agreement with that obtained from the optical microscopy. In the right δ interval, we fit the data points to a second degree polynomial, as shown in Figure 2b. Since, there are few points in this interval, the extrapolated value is affected by a large uncertainty, and μ_6 cannot be calculated. Notwithstanding, the linear term gives $\mu_4 = (1.1 \pm 0.4) \times 10^{-21} \text{ m}^4$ which coincides, within the experimental error, with the measured one. The obtained D value is used as an input parameter in the direct method for determining the volume fraction distribution. In Figure 3, the resulting distribution is compared with the one obtained by optical microscopy measurements. It is clear from that figure the complete superimposition of the NMR and optical microscopy results. Please note that in order to evaluate the distribution function by NMR

measurements in ref 15, a log-normal distribution was assumed. If this assumption is accepted, knowing μ_2 and μ_4 , the distribution parameters can be immediately evaluated.¹⁰

As far as the xylene emulsion is concerned, the δ_b value is so small that only eq 9 can be applied. Therefore the proposed method has to be used to determine the D coefficient and thus $\Phi(R)$. Figure 4a shows the best fit curve (third degree polynomial) which gives $\chi_{\text{exp}} = 8.63$. Figure 4b graphically reproduces the results obtained applying the direct method for different and arbitrary D values. Since Δ is kept constant throughout the whole experiment, the trend of χ against D^{-1} is a straight line. The intersection between the experimental line and the theoretical line is $D = (2.0 \pm 0.4) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, close to the true diffusion coefficient of the neat liquid reported in the literature.¹³ The $\Phi(R)$ corresponding to this value of D is shown in Figure 5, where one can, once again, see the excellent agreement with the situation seen by optical microscopy.

Conclusions

This paper completes the testing of our general approach to evaluate the droplets' polydispersity and the dispersed phase self-diffusion coefficient in emulsion systems directly from the echo attenuation of a PGSE-NMR experiment without any a priori assumption. The aim of this paper is to test our proposed method even in the case of emulsions characterized by small dimensions of the dispersed phase aggregates. The term small has to be referred to the quantity $\sqrt{\Delta\delta}$ and it is therefore relative to both experimental conditions and the nature of the sample. When this is the case, the experimental data coming from a PGSE-NMR measurement lay on the right-hand side of a limiting δ value. To get from these data both the D coefficient and the moments of distribution function of the dispersed phase, the new proposed computational method proved to be reliable in all of the conditions tested.

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