

PFG NMR Study of Polymer and Solubilizate Dynamics in Aqueous Isotropic Mesophases of Some Poloxamers

Harald Walderhaug*

Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway

Received: December 9, 1998; In Final Form: February 25, 1999

The self-diffusion of the polymer and oil (i.e., *tert*-butylbenzene) components in aqueous ternary cubic liquid crystalline (clc) mesophases formed by three different Pluronic triblock copolymers (i.e., P94, F68, and F127) has been investigated using pulsed-field gradient (PFG) NMR. For the polymer chains, the diffusion has been compared to that determined in corresponding aqueous binary (without oil) clc mesophases and micellar solution phases. The polymer chain diffusion is Fickian (i.e., Gaussian) in the micellar solution state and becomes anomalous in the clc mesophases. A pronounced departure from a single-exponential spin-echo attenuation of the polymer chains in the clc mesophases is observed. The self-diffusion of the oil component in the ternary clc mesophases is Fickian. Compared to the self-diffusion of the pure oil at the same temperature, it is found that the diffusion is reduced by a factor of 10^3 in the clc mesophases. This clearly demonstrates that the clc mesophases consist of closed aggregates with the oil solubilized in the micelles. A possible scenario for the observed polymer chain and the oil diffusion behavior is discussed, based partly on PFG NMR results obtained from a binary aqueous clc sample of the surfactant dodecyl trimethylammonium chloride (DOTAC).

Introduction

Triblock copolymers of the type POE–POP–POE, where POE denotes identical poly(oxyethylene) blocks and POP denotes a poly(oxypropylene) block, generally called poloxamers and commercially available from BASF Corp. under the trade name Pluronics, have attracted interest from industry^{1,2} as well as from academia.^{3–7} Dissolved in water, these polymers are organized into micelles above concentration and temperature limits that depend on the composition of the chains. This self-assembly behavior results from the fact that the POP block has a lower solubility in water as compared to the two POE blocks. The water solubility decreases faster for the former than for the two latter blocks as temperature is raised. At low temperatures, therefore, the water solutions may consist of molecularly dispersed material up to quite high concentrations. Above a certain concentration-dependent temperature micelles are formed. These aggregates are organized with the POP blocks forming the core, thereby preventing the thermodynamically unfavorable contact between these segments and water. The POE blocks form a corona of solubilized POE segments. See, e.g., ref 7 and references therein for further details.

Above a certain concentration (typically >20 wt %), the micellar phase may undergo a transition to a “gel” phase.⁸ Small-angle neutron scattering results^{8,9} on aqueous Pluronic systems suggest that the so-called gels consist of close-packed arrays of micelles of nearly the same size as those in the corresponding micellar phase. Some studies^{10–13} indicate that a further temperature increase eventually leads to a breakdown of the gel structure, again resulting in a solution of low viscosity, and the system returns to a micellar state. The temperature range for the “gel” zone depends on the concentration and on the composition of the Pluronic copolymer.¹⁴

Recently, a number of studies addressing the structure of the various “gel” phases formed by Pluronic systems have been performed.^{15–23} Using various experimental and also theoretical

methods it has been possible to draw the conclusion that the “gels” in fact are cubic liquid crystalline (clc) mesophases with the micelles close-packed in, e.g., a primitive or a body-centered cubic symmetry. In a recent work by Zhang and Khan,²⁴ the phase behaviors of several binary aqueous Pluronic systems were investigated as a function of Pluronic molecular weight, molecular composition (defined as f = the degree of polymerization of the two POE blocks relative to that for the central POP block), and, for each Pluronic system, the sample composition and temperature. In general, in the polymer concentration range 40–80 wt % hexagonal and lamellar liquid crystalline phases are formed over a large temperature range. At lower polymer concentrations, a micellar solution phase is formed. Depending on molecular weight there might be formed a clc phase between the micellar solution phase and the hexagonal phase, in a typical concentration range of 20–40 wt %. A main conclusion from this work is that the Pluronic polymers in general behave as nonionic surfactants. The Pluronic P94 system (see below) was critically examined in Zhang and Khan’s work. Here, a clc phase was found in the above-mentioned concentration range, for temperatures between 25 and 45 °C. For Pluronics F68 ($f = 5.0$) and F127 ($f = 2.9$)⁷ (see below), a clc phase is expected between a micellar solution phase and a hexagonal liquid crystalline phase, analogous to the phase behavior pattern of the P94 system.²⁴

We have at our lab conducted a number of studies of an aqueous Pluronic system, i.e., Pluronic F68, using dynamic light scattering (DLS), pulsed-field gradient (PFG) NMR, and rheology.^{25–29} Very complex polymer chain dynamics is revealed as the clc zone is entered by increasing the temperature to 37 °C for a 35 wt % sample. PFG spin-echo attenuation data show a very pronounced departure from a single exponential when entering the cubic zone. Time-resolved PFG experiments show that the self-diffusion process gradually departs from a Fickian (i.e., Gaussian) nature in the micellar solution state to a non-Fickian (anomalous) nature in the

corresponding cubic zone.^{27,29} In a complementary work,³⁰ some further time-resolved PFG results for a clc sample of the binary aqueous Pluronic P94 system are presented.

In this work, time-resolved PFG results for both the polymer and oil components in the corresponding clc phase of some ternary Pluronic/oil/water systems will be presented. Aqueous Pluronic systems solubilize especially aromatic hydrocarbons.^{7,14} *tert*-Butylbenzene (tBb) was chosen as the oil component. This oil has a very low water solubility and can be assumed to be well solubilized in the Pluronic micelles. The presence of solubilized oil affects the phase behavior of the systems somewhat,¹⁴ but for the systems covered in this work we can assume that the samples investigated are located in the stable one-phase clc region that exists for the corresponding binary systems. The Pluronic systems were P94, F68, and F127 (see below). Also, time-resolved PFG results obtained from a clc phase of a binary aqueous ionic surfactant system, i.e., dodecyl trimethylammonium chloride (DOTAC)/water will be presented. A comparison between the PFG results for all these systems will shed light on the actual dynamic state of the Pluronic copolymer chains in the clc structure referred to above.

Theoretical Considerations

The PFG NMR technique is well established^{31–36} and has been used to determine self-diffusion coefficients in the range 10^{-9} – 10^{-14} m² s⁻¹ for liquid systems. The method consists of labeling nuclear spins by their Larmor precession frequencies in a spatially varying magnetic field. In the so-called “narrow pulse approximation” ($\delta \ll \Delta$; see below) the attenuation of the spin–echo on applying the field gradient pulse of magnitude g is given by³⁷

$$\psi = \int \rho(r) \int P_S(r|r', \Delta) \exp[i\gamma g \delta(r' - r)] dr' dr \quad (1)$$

where γ denotes the gyromagnetic ratio of the nucleus under consideration (the ¹H nucleus here). Δ is the separation of the gradient pulses and has the status of the physical observation time of the diffusive process for the spins. δ is the duration of the gradient pulses. $\rho(r)$ denotes the static spin density function. $P_S(r|r', \Delta)$ is the self-correlation function,³⁶ also called the propagator, which gives the probability that a spin initially at position r at time zero will move to position r' at time Δ .

For nuclear spins undergoing a Brownian random walk characterized by a self-diffusion coefficient D , the propagator has a simple Gaussian form. In the narrow pulse approximation eq 1 reduces to

$$\psi = \exp[-(1/2)(\gamma g \delta)^2 \langle z^2 \rangle] \quad (2)$$

where $\langle z^2 \rangle$ is the mean-square nuclear displacement along the magnetic field gradient direction and can be written as

$$\langle z^2 \rangle = 2D\Delta \quad (3)$$

Equation 2 is, however, suggested to be more general in that it may also describe anomalous (i.e., non-Gaussian) diffusion.³⁸

In principle, PFG NMR may be considered to be mathematically equivalent to a scattering experiment.^{36,39} The intermediate incoherent scattering function of the protons in the polymer molecules is measured, and in the free diffusion limit the echo attenuation function may be expressed as

$$\psi = \exp(-q^2 D \Delta) \quad (4)$$

with a generalized q -space vector $\mathbf{q} = \gamma g \delta$. The maximum value of the \mathbf{q} vector is of the order of 10^7 m⁻¹ in pulsed-field gradient

experiments, yielding a lower limit of about 100 nm for the space scale probed.

In some situations, the mean-square displacement may be described by the following relation:^{27,38}

$$\langle z^2(t) \rangle \propto t^\alpha \quad (5)$$

with $\alpha < 1$, which represents a generalization of the Einstein equation (eq 3). These situations include fractal-type diffusion in disordered media where the exponent α may be interpreted in terms of a random walk fractal dimension $d_w = 2/\alpha$ (see ref 27 and references therein).

Other theoretical models predict certain values for the power law exponent α . The dynamics of short and long polymer chains in melts or in concentrated solutions may be described in the framework of the following models. For short chains, the dynamics in the Rouse limit⁴⁰ (hydrodynamic interactions are ignored) is governed by the Rouse time τ_R (the time it takes for a chain to diffuse a distance of the order of its radius). For times much longer than τ_R , we expect ordinary center-of-mass diffusion to occur ($\alpha = 1$). At times $t < \tau_R$, only a portion of the chain will have diffused and the mean-square displacement of this internal type of motion is predicted to become proportional to $t^{0.5}$. For long chains, the dynamics of entangled polymer molecules is often in terms of the tube/reptation model.^{41,42} The reptation of sufficiently long chains is characterized by a one-dimensional Rouse-like⁴² curvilinear diffusive motion in a one-dimensional tube formed by the topological constraints of the surrounding chains. Several characteristic time constants enter the description of the chain dynamics in this model. Suffice it to say that for very short times when free Rouse motion prevails, and for a time interval when curvilinear diffusion in the tube is probed, a power law exponent $\alpha = 0.5$ is again predicted.

In the case of observed Fickian diffusion, the observed self-diffusion coefficient, D_{obs} , may be interpreted within a two-sites scenario. For molecules that may be present either as freely diffusing entities with diffusion coefficient D_f or in an aggregate with diffusion coefficient D_b , these coefficients are related in the following way:

$$D_{\text{obs}} = p_f D_f + (1 - p_f) D_b \quad (6)$$

for a situation where fast exchange of the molecules between the two sites on the NMR time scale (i.e., Δ) prevails.⁴³ p_f denotes the fraction of molecules present in the free state.

Experimental Section

Materials and Sample Preparations. Pluronic P94 (composition E₂₈P₄₈E₂₈, molecular weight (M) \approx 5300),¹⁰ F68 (composition E₇₆P₃₀E₇₆, $M \approx$ 8400), and F127 (composition E₉₉P₆₉E₉₉, $M \approx$ 12600),⁷ E and P denoting oxyethylene and oxypropylene segments, respectively, and the subscripts denoting the number of segments in the blocks, were obtained from BASF. The Pluronic P94 was purified by repeated recrystallization in *n*-hexane.¹⁰ The degree of polydispersity of Pluronic polymers is known to be small. The polydispersity index M_w/M_n (M_w and M_n denoting weight and number average molecular weights, respectively) is usually less than 1.10.⁴⁴ Chemical heterogeneities such as, e.g., diblock polymers, may, however, exist in Pluronic samples. The recrystallization procedure in hexane is used to remove such impurities. *tert*-Butylbenzene (puriss grade) was from Fluka and used as received. Dodecyl trimethylammonium bromide (DOTAB), from Fluka, was converted to the hydroxide form by ion exchange on Dowex 21K (Fluka). The DOTAOH was then neutralized with HCl to

the corresponding chloride salt, denoted DOTAC, according to a well-known recipe.⁴⁵ The product was thereafter freeze-dried. The Pluronic solutions were prepared by weighing the materials, and the samples were stirred until they were homogeneous. They were then transferred to 5 mm NMR tubes. At 30 °C and at the compositions given in the Results and Discussion section, the samples were transparent and stiff. They were all judged to be clc mesophases. The DOTAC sample (50 wt %) was prepared by weighing the components in a glass tube that was sealed. This tube was then heated to ca. 100 °C until the sample was homogeneous (micellar phase), and upon cooling to room temperature, a clc phase (I₁) was formed.⁴⁶ The sealed sample was left for 2 weeks to ensure equilibrium and was thereafter transferred to a 5 mm NMR tube. The water was deionized and distilled.

NMR Measurements. All NMR experiments were carried out in 5 mm NMR tubes with the aid of the PFG NMR technique³⁴ on a Bruker DMX-200 spectrometer utilizing stimulated echoes.^{35,47} A so-called “pre-emphasis adjustment” of the magnetic field gradient pulse shape was applied in order to avoid eddy current effects on the echoes. The attenuation of the echo amplitude was sampled as a function of the magnitude, g , of the applied gradient pulse ($0.5 \leq g \leq 8$ T/m).

The gradient delivery system is completely electronically controlled. The field gradients for the experimental setup with the actual probehead interfaced have been calibrated by the manufacturer. The pulse duration δ was kept constant at each experimental run and was typically 3 or 4 ms. In this way, the narrow pulse approximation, i.e., $\delta \ll \Delta$, was always fulfilled. The time window available to the PFG NMR method is determined by the gradient amplitude and by spin relaxation. For the present systems, it is limited to $0.1 \text{ s} \leq \Delta \leq 3 \text{ s}$. The measurements were performed between 10 and 65 °C. By use of a variable temperature control unit, the temperature constancy was better than ± 0.5 °C. The temperature settings were calibrated by using an ethylene glycol sample, giving easily measurable shift differences between the two proton signals that depend strongly on temperature.

The PFG experiments were performed in the Fourier transform mode,³⁴ permitting access to correct spin–echo intensity when more than one component contributes to this intensity. For *tert*-butylbenzene, the proton signal from the phenyl group was utilized, since this signal does not interfere with proton signals from the Pluronic molecules (the signals from the POP methyl group and that from the methyl groups in the *tert*-butyl group overlap). For the Pluronic molecules, the POE proton signal at ca. 4 ppm was utilized.

In the optically isotropic clc mesophases static dipolar interactions between the protons are absent, due to symmetry reasons.⁴⁸ Therefore, high-resolution NMR spectra are obtained from these samples.

Results and Discussion

Polymer Diffusion. The phase behavior of the binary system Pluronic P94/water has been summarized elsewhere.²⁴ At concentrations between 24 and 39 wt % polymer and a temperature between ca. 20 and 45 °C, a cubic liquid crystalline (clc) phase is formed. Due to the existence of this mesophase between a micellar solution phase at lower and a hexagonal liquid crystalline phase at higher polymer concentration, it seems reasonable to suggest that this clc phase consists of micelles packed in a cubic (e.g., primitive or body-centered) lattice.²⁴ PFG NMR results for the clc phase of this two-component system will be published in a separate paper.³⁰ A central result is found in Table 1.

TABLE 1: Dynamic Parameters for the Polymer and *tert*-Butylbenzene (tBb) Components in the Cubic Liquid Crystalline Phases of the Three Pluronic Systems at 30 °C and the Diffusion Coefficients for Pure tBb and the Dodecyl Trimethylammonium Chloride (DOTAC) Surfactant in the clc Phase of that System

system	α (mean) ^a	D (tBb or DOTAC) ^a
P94/tBb/water	0.50 ± 0.10	$1.38 (\pm 0.01) \times 10^{-12}$
F68/tBb/water	0.45 ± 0.05	$3.09 (\pm 0.08) \times 10^{-12}$
F127/tBb/water	not determined	$1.80 (\pm 0.02) \times 10^{-12}$
pure tBb		$8.60 (\pm 0.18) \times 10^{-10}$
P94/water ^b	0.58 ± 0.10	
F68/water ^c	0.50 ± 0.05	
DOTAC/water ^d	0.99 ± 0.01	$6.05 (\pm 0.03) \times 10^{-13}$

^a See text. Diffusion coefficients in units of $\text{m}^2 \text{s}^{-1}$. ^b See also ref 30. ^c Temperature, 37 °C; see ref 27. ^d Temperature, 25 °C.

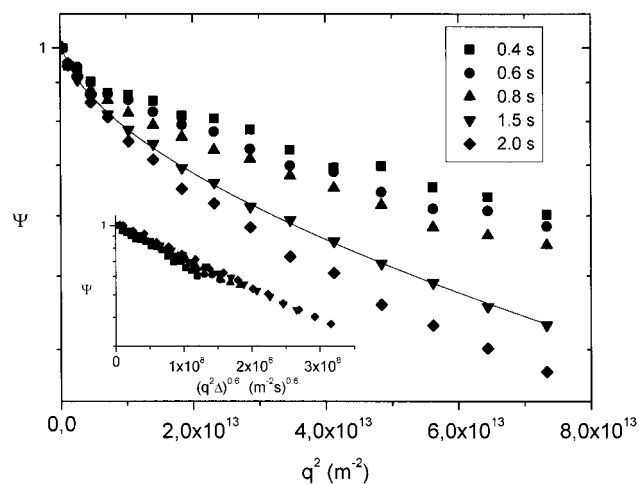


Figure 1. Polymer spin–echo attenuation vs q^2 (see text) for Pluronic P94 in the ternary clc phase at 30 °C at the values for the observation time Δ given in the figure. The curve through one of the data sets represents the fit of the set to eq 7. The insert figure displays the same data plotted vs $(q^2 \Delta)^{0.6}$.

As stated in the Introduction, Pluronic systems are able to solubilize aromatic hydrocarbons (oils) to a high degree. PFG spin–echo attenuation data for the polymer chains in the system P94/*tert*-butylbenzene/water, at an oil/polymer mole ratio of 8, a polymer concentration of ca. 30 wt %, and a temperature of 30 °C, is shown in Figure 1. As for the corresponding binary system, the echo attenuation may be described by a generalization of eq 4, viz. a stretched exponential relation of the following form:⁴⁹

$$\psi = \exp(-(q^2 \Delta D)^\beta) \quad (7)$$

It should be stated here that this relation is purely empirical. D is an effective (apparent in the case of anomaly) diffusion coefficient, and the empirical parameter β ($0 < \beta \leq 1$) is a measure of the departure from a single-exponential spin–echo decay ($\beta < 1$). This stretched exponential exponent is not to be confused with the anomalous time exponent which has its origin in theoretical arguments (see above). A value of $\beta < 1$ might signify a distribution of diffusivities that has its origin in some kind of heterogeneity in the system or it may also signify a non-Fickian diffusion process. Fits of the various spin–echo attenuation data sets for each value of the observation time Δ (see Figure 1) to eq 7, produce values of β ca. 0.6. In the insert figure are plotted the same data versus $(q^2 \Delta)^{0.6}$. The near condensation of the data indicates a value for the anomalous time exponent α in the neighborhood of this value (see eqs 2

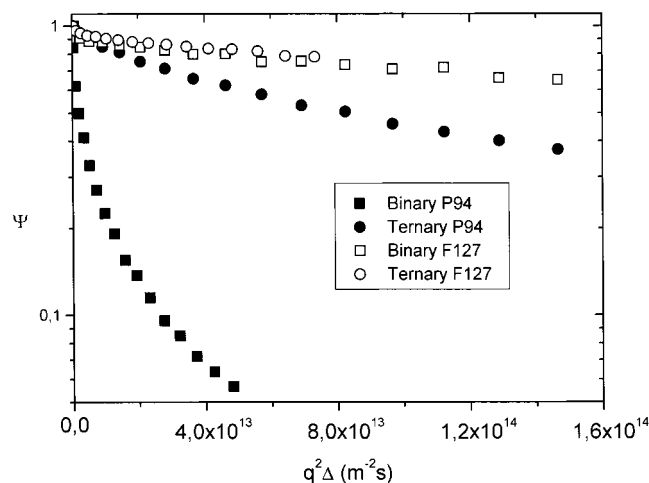


Figure 2. Polymer spin-echo attenuation data for the four clc systems indicated in the figure. For the binary F127 system the temperature was 65 °C. For the other systems the temperature was 30 °C.

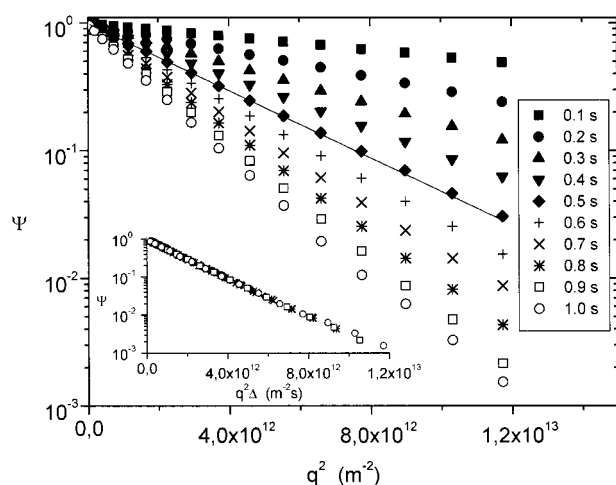


Figure 3. Surfactant spin-echo attenuation data for the clc phase of the binary aqueous system dodecyl trimethylammonium chloride (DOTAC) at 50 wt % DOTAC and a temperature of 25 °C at the values for Δ as given in the figure. The line through one of the data sets represents a fit of the set to eq 4. In the insert figure are displayed the same data plotted vs $q^2\Delta$.

and 5), since Δ is raised to an exponent also in this rough approach. By utilizing the same procedure as that of ref 27 (see Figure 3 therein), values for α in the range 0.36 to 0.48 are determined. The α value in Table 1 for this system represents a mean value from both these procedures. The error limit covers the range of determined values for the anomalous time exponent.

An analogous procedure for the evaluation of corresponding data from the ternary Pluronic/oil/water cubic phases of Pluronic F68 produces the α values found in Table 1. The value for α (i.e., 0.45) is practically identical with that for the corresponding P94 system within its precision. Also, comparing the α values found for the ternary P94 and F68 systems to the values for this parameter in the corresponding binary systems (see Table 1), they are all found to be identical, within precision, and close to 0.5. For the F127 binary and ternary clc systems, the attenuation is too low to allow for quantitative data evaluation. This is illustrated in Figure 2, where a comparison is made between typical polymer echo attenuation data from the binary and ternary F127 clc systems and the corresponding P94 systems. For the binary F127 system, a temperature of 65 °C and an observation time $\Delta = 2.0$ s was needed to produce even this minute attenuation.

As indicated in Figure 2 there is a clear difference in polymer mobility in the two P94 clc phases investigated, as judged from the different decay rates of the spin-echo attenuation data for these two systems. In qualitative terms it can be stated that the polymer mobility is higher in the binary than in the corresponding ternary system for P94. This is not a general conclusion, however. The polymer mobility in the F68 system is hardly influenced by the presence of oil (data not shown).

To probe a possible difference in the dynamic state of the molecules between the cubic structure of the phases encountered in this work and that of another well-known cubic system, corresponding spin-echo attenuation experiments inside the cubic phase I₁ of the system dodecyl trimethylammonium chloride (DOTAC)/water at a composition of 50 wt % surfactant and a temperature of 25 °C was conducted. This cubic phase consists of elongated micelles close-packed in a simple (primitive) cubic lattice.⁵⁰ The spin-echo attenuation data are presented in Figure 3. As is clearly revealed, the attenuation data at all the investigated diffusion times are exponential, corresponding to a single diffusivity. This is explicitly shown by a fit of one of the data sets to eq 4, illustrated by the line through these data. Also, plotted as a function of $q^2\Delta$, these data perfectly condense to a master curve, as illustrated in the insert to Figure 3. A diffusion coefficient D for the surfactant molecules of ca. $6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ is extracted from these data (see Table 1).

The simple Fickian diffusion process observed for the surfactant molecules in this cubic system may be rationalized within the two-sites model described above. The surfactant molecules are present either in the micelles and diffusing with this kinetic entity with a diffusion coefficient D_b or are diffusing as free monomers characterized by a diffusion coefficient D_f . A state of fast exchange between these two sites can safely be assumed for the surfactant molecules.⁵¹ The fraction of free surfactant molecules, p_f (see eq 6), may be estimated from the known value of the critical micelle concentration (cmc) of $2.0 \times 10^{-3} \text{ M}$.⁵² At a concentration of 50 wt %, p_f will be ca. 1.2×10^{-3} . The diffusion coefficient for free DOTAC cations in water is expected to be close to $5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, since this value is inferred from measurements on sodium dodecyl sulfate (SDS) well below its cmc.⁵³ Putting these values for the various parameters into eq 7, a value of $D_{\text{obs}} = 6.0 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ is predicted, in good agreement with the experimental value. It is assumed that the contribution to the diffusivity from the second term in eq 7 is zero. This means that the diffusion of the micelles in the cubic liquid crystalline phase is below the detection limit for our equipment.

Returning to the Pluronic F68 and P94 clc systems, these behave qualitatively differently regarding the diffusion process. First, as clearly revealed by the data in Figure 1, the attenuation is nonexponential and may be described by a stretched exponential relationship, eq 6. The stretched character of the echo attenuation is larger in the cubic phase than that observed for the corresponding micellar state. As an example, for the 30 wt % P94 system at 10 °C, in the micellar solution state,¹⁰ the stretched exponential exponent β is ca. 0.80, and a mean value for the anomalous exponent α is 0.87 ± 0.05 , which is close to the Fickian value of 1; see eq 5 (data not shown) and ref 27. This points to a possibility that the exchange of Pluronic molecules, in the micellar solution, between the free state and the bound (to the micelles) state is slow and of the order of or longer than the physical observation time, Δ .⁴³ This conclusion is, however, not in line with that based on ultrasound experiments on aqueous Pluronic systems by Michels et al.²³ They

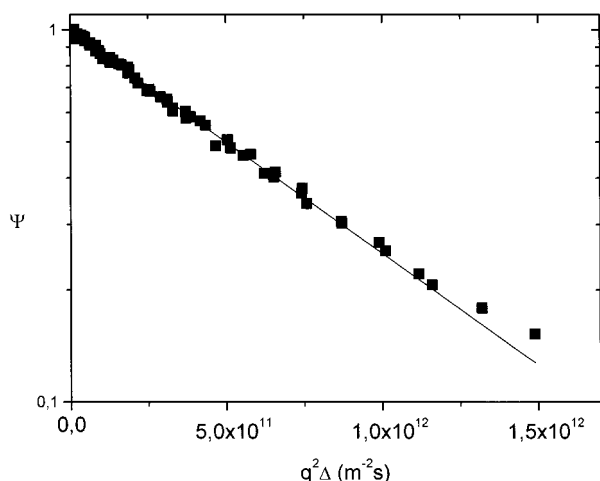


Figure 4. Spin-echo attenuation for *tert*-butylbenzene for several values of Δ in the range 0.1–1.0 s, plotted vs $q^2\Delta$. The line through the data represents the fit of all these data to eq 4; see Table 1.

concluded that the exchange time of Pluronic molecules between micelles is of the order of microseconds, which is fast compared to the NMR time scale.

For the Pluronic polymers in the clc state the observed diffusion process is anomalous and can therefore not be rationalized within the above two-sites model which is based on the assumption that both the free and bound states show Gaussian dynamics. However, in qualitative terms it may be stated that the observed mobility is probably dominated by the micellar (bound) diffusion. Support for this view is given by the spin-echo attenuation data obtained from the two clc samples of Pluronic F127, displayed in Figure 2. It appears that the diffusion of the micelles in these two systems is below the detectability limit of our present equipment, as was also the case for the DOTAC clc system discussed above. For the F68 and P94 systems, the observed spin-echo attenuation may be ascribed to hindered diffusion of micelles in the clc phase, producing the observed anomaly ($\alpha < 1$).

Oil Diffusion. In Figure 4 are shown spin-echo attenuation data for *tert*-butylbenzene (tBb) for several values of Δ in the clc sample of P94 at 30 °C. As can be seen in the figure, the echo attenuation data for tBb condense to a straight line when plotted vs $q^2\Delta$, as predicted by eq 4. This means that the diffusion of the oil component is Fickian. The diffusion coefficient is found in Table 1.

For the corresponding F127 and F68 clc samples, the same result for the oil diffusion is found as for the P94 system presented above. The oil diffusion is Fickian, and the diffusion coefficient was found to be of the same order of magnitude ($10^{-12} \text{ m}^2 \text{ s}^{-1}$). The oil diffusion coefficient for the F68 system is somewhat higher than that for the two other systems (see Table 1).

Compared to the diffusion coefficient of the pure tBb oil at 30 °C which was measured to be of the order of $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (see Table 1), the diffusion of this component in the above presented ternary systems is a factor of the order of 10^3 slower. This means that the aggregates formed are of the oil-in-water type with the oil solubilized in the micelles formed by the Pluronic polymers.¹⁴ However, the results presented in this work clearly reveal the different dynamic state of the oil and polymer components. The oil diffusion is Fickian, whereas the polymer diffusion is non-Fickian. The oil molecules seem to have some translational freedom which the polymer molecules lack. In the time window that the systems are observed (Δ is a few tenths

of a second; see above), the oil molecules on the average visit many micelles. In this context it should be noted that clc phases of binary Pluronic/water systems are formed when the volume fraction Φ of the spherical micelles has reached the critical value of 0.53.⁵⁴ At this value for Φ the micelles are close-packed (see also the Introduction). Hydrodynamic radii for the micelles in the corresponding aqueous binary systems of the Pluronic polymers used in this work are of the order of 10 nm.⁷ Low water solubility for the oil most probably prevents oil diffusion through the intervening solvent. A possible oil diffusion pathway consisting of contact points formed where different micelles touch each other may be conceived.

Concluding Remarks

The polymer chain diffusion has been investigated using pulsed-field gradient (PFG) NMR for three Pluronic polymers, i.e., Pluronic P94, F68, and F127, in aqueous binary and ternary (solubilized aromatic hydrocarbon) cubic liquid crystalline (clc) mesophases. A comparison has been made with PFG results for the polymer chain diffusion in corresponding binary micellar solution phases. It is found that the polymer chain self-diffusion process is Fickian or close to Fickian for these latter states but becomes anomalous when the clc state is entered. The degree of anomaly, as measured by the anomalous time exponent α (eq 5), is found to be around 0.5 for the polymers in the clc phases of the F68 and P94 systems. For the polymer in the clc phases of F127 it could not be measured due to low spin-echo attenuation. It is suggested that the observed polymer diffusion reflects the mobility of the micellar aggregates comprising the clc phases.

For the oil component, i.e., *tert*-butylbenzene (tBb), the diffusion is found to be Fickian. A 10^3 -fold decrease for the diffusion coefficient measured in the clc phases compared to that for the pure oil at the same temperature indicates closed micellar aggregates in the clc phases, with the oil solubilized in the micelles. The dynamic state of the oil molecules is suggested to be rationalized within a scenario where the oil molecules utilize the contacts between the micelles in the clc phases.

Acknowledgment. The author of this article thanks Dr. Balin Balinov, Nycomed Amersham, Inc., Oslo, for stimulating discussions during the preparation of the manuscript which has improved in quality due to his valuable comments.

References and Notes

- (1) Tuzar, Z.; Kratochvil, P. In *Surface and Colloid Science*; Matijevic', E., Ed.; Plenum Press: New York, 1993.
- (2) Schmolka, I. R. In *Polymers for Controlled Drug Delivery*; Tarcha, P. J., Ed.; CRC Press: Boca Raton, 1991; p 189.
- (3) Chu, B. *Langmuir* **1995**, *11*, 414.
- (4) Almgren, M.; Brown, W.; Hvidt, S. *Colloid Polym. Sci.* **1995**, *273*, 2.
- (5) Alexandridis, P.; Hatton, T. A. *Colloids Surf., A: Physicochem. Eng. Aspects* **1995**, *96*, 1.
- (6) Mortensen, K. *J. Phys.: Condens. Matter* **1996**, *8*, A103.
- (7) Chu, B.; Zhou, Z. In *Nonionic Surfactants, Polyoxyalkylene Block Copolymers, Surfactant Sci. Ser.*; Nace, V. M., Ed.; 1996; Vol. 60, p 67.
- (8) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Colloid Polym. Sci.* **1990**, *268*, 101.
- (9) Mortensen, K.; Brown, W.; Nordén, B. *Phys. Rev. Lett.* **1992**, *68*, 2340.
- (10) Hvidt, S.; Jørgensen, E. B.; Brown, W.; Schillén, K. *J. Phys. Chem.* **1994**, *98*, 12320.
- (11) Brown, W.; Schillén, K.; Hvidt, S. *J. Phys. Chem.* **1992**, *96*, 6038.
- (12) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145.
- (13) Alexandridis, P.; Zhou, D.; Khan, A. *Langmuir* **1996**, *12*, 2690.
- (14) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, *25*, 5440.

- (15) Jørgensen, E. B.; Jensen, J. H.; Hvidt, S. *J. Non-Cryst. Solids* **1994**, 172–174, 972.
- (16) Muller, R.; Gérard, E.; Dugand, P.; Rempp, P.; Gnanou, Y. *Macromolecules* **1991**, 24, 1321.
- (17) Mortensen, K.; Talmon, Y. *Macromolecules* **1995**, 28, 8829.
- (18) Hoffmann, H.; Ulbricht, W. *Curr. Opin. Colloid Interface Sci.* **1996**, 6, 726.
- (19) Prud'homme, R. K.; Wu, G.; Schneider, D. K. *Langmuir* **1996**, 12, 4651.
- (20) Zhou, D.; Alexandridis, P.; Khan, A. J. *Colloid Interface Sci.* **1996**, 183, 339.
- (21) Schillén, K.; Glatter, O.; Brown, W. *Prog. Colloid Polym. Sci.* **1996**, 93, 66.
- (22) Noolandi, J.; Shi, A.-C.; Linse, P. *Macromolecules* **1996**, 29, 5907.
- (23) Michels, B.; Waton, G.; Zana, R. *Langmuir* **1997**, 13, 3111.
- (24) Zhang, K.; Khan, A. *Macromolecules* **1995**, 28, 3807.
- (25) Nyström, B.; Walderhaug, H.; Hansen, F. K. *Faraday Discuss.* **1995**, 101, 335.
- (26) Nyström, B.; Walderhaug, H. *J. Phys. Chem.* **1996**, 100, 5433.
- (27) Walderhaug, H.; Nyström, B. *J. Phys. Chem. B* **1997**, 101, 1524.
- (28) Nyström, B.; Kjøniksen, A.-L. *Langmuir* **1997**, 13, 4520.
- (29) Walderhaug, H.; Nyström, B. *Trends Phys. Chem.* **1997**, 6, 89.
- (30) Walderhaug, H. To be published in AIP Conference series.
- (31) Stejskal, E. D.; Tanner, J. E. *J. Chem. Phys.* **1965**, 42, 288.
- (32) von Meerwall, E. D. *Adv. Polym. Sci.* **1983**, 54, 1.
- (33) Callaghan, P. T. *Aust. J. Phys.* **1984**, 37, 359.
- (34) Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, 19, 1.
- (35) Kärger, J.; Pfeifer, H.; Heink, W. *Adv. Magn. Reson.* **1988**, 12, 1.
- (36) Callaghan, P. T. *Principles of Nuclear Magnetic Resonance Microscopy*; Oxford University Press: New York, 1991.
- (37) Stejskal, E. D. *J. Chem. Phys.* **1965**, 43, 3597.
- (38) Kärger, J.; Pfeifer, H.; Vojta, G. *Phys. Rev. A* **1988**, 37, 4514.
- (39) Fleischer, G.; Fajara, F. *NMR Basic Princ. Prog.* **1994**, 30, 159.
- (40) Daoud, M. In *Fractals in Science*; Bunde, A., Havlin, S., Eds.; Springer-Verlag: Berlin/Heidelberg, 1994.
- (41) De Gennes, P.-G. *J. Chem. Phys.* **1971**, 55, 1972.
- (42) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
- (43) Kärger, J.; Ruthven, D. M. In *Diffusion in Zeolites and Other Microporous Solids*; John Wiley & Sons: New York, 1992.
- (44) Whitmarsh, R. H. In *Nonionic Surfactants, Polyoxyalkylene Block Copolymers, Surfactant Sci. Ser.*; Nace, V. M., Ed., 1996; Vol. 60, p 1.
- (45) Khan, A.; Fontell, K.; Lindblom, G. *J. Phys. Chem.* **1982**, 86, 383.
- (46) Balmbra, R. R.; Clunie, J. S.; Goodman, J. F. *Nature* **1969**, 222, 1159.
- (47) Burstein, D. *Concepts Magn. Reson.* **1996**, 8, 269.
- (48) Charvolin, J.; Rigny, P. *J. Chem. Phys.* **1973**, 58, 3999.
- (49) Nyström, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, 97, 7743.
- (50) Lindblom, G.; Orädd, G. *Prog. Nucl. Magn. Reson. Spectrosc.* **1994**, 26, 483.
- (51) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, W.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, 80, 905.
- (52) Mukerjee, P.; Mysels, K. J. In *Critical micelle concentrations of aqueous surfactant systems*; NSRDS-NBS 36; U.S. Government Printing Office: Washington, DC, 1971.
- (53) Walderhaug, H.; Nyström, B.; Hansen, F. K.; Lindman, B. *J. Phys. Chem.* **1995**, 99, 4672.
- (54) Mortensen, K.; Pedersen, J. K. *Macromolecules* **1993**, 26, 805.