Spontaneous Size Selection in Cholesteric and Nematic Emulsions

T. Tixier,^{†,§} M. Heppenstall-Butler,[‡] and E. M. Terentjev^{*,†}

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K., and Corporate Research, Unilever R&D, Colworth House, Sharnbrook, Bedford MK44 1LQ, U.K.

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We study the spontaneous size selection in lyotropic cholesteric (W/O) and thermotropic nematic (O/W) liquid crystal emulsions. The droplet sizes have been characterized by dynamic light scattering, which indicates a narrow monomodal distribution of droplets achieved spontaneously even without emulsion filtration. Anchoring of the director, provided by the chosen surfactant on the interface, may generate a topological defect inside the droplet. Below the critical radius $R^* = K/W$, determined by the ratio of Frank elastic and the surface anchoring constants, the effective anchoring strength is weak and droplets are not topologically charged; this allows them to coalesce freely, depleting the size distribution in this range. Large droplets possess a topological charge of +1 and present a high elastic energy barrier for pair coalescence; the resulting size distribution is skewed, with $R > R^*$, and effectively frozen.

1. Introduction

The physics and chemistry of colloids and emulsions is a subject rapidly evolving from an empirical science into an important domain of fundamental research.¹ A range of new application possibilities has emerged from the fundamental studies of complex fluids with internal degrees of freedom and symmetry breaking.² For example, the problem of controlled encapsulation and release is clearly of paramount importance to a wide range of applications in the area of pharmaceutics, foods, or personal care.

The traditional emulsions are composed of oil droplets dispersed in a continuous water phase (O/W) (direct emulsion) or of water droplets in an oil phase (W/O) (inverse emulsion). To prepare a stable emulsion of macro- or mesoscopic droplets, there must be a surface active material present to protect the newly formed droplets from immediate coalescence. The addition of surfactant is also essential in order to reduce the interfacial tension between two liquids so that the emulsion can be broken down further. However, there is an understanding, quite general for colloids and emulsions, that their structural stability is a kinetic concept and not a thermodynamic one.^{3,4} This means that when the reduction of interface energy is not able to compensate for the loss in conformational entropy on droplet aggregation, the only thermodynamic equilibrium is the full phase separation. When, at a very low surface tension, the entropic part of the free energy demands the two phases break into a fine dispersion, a micromicellar solution results. For long-term emulsion stability against coalescence and resulting phase separation, the mechanical strength of the interfacial film formed by a surface-active substance is more important than its effect on interfacial tension.^{5,6}

* To whom correspondence should be addressed. E-mail: emt1000@ cam.ac.uk.

[‡] Corporate Research, Unilever R&D.

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In our work, we investigate emulsions in which the dispersed phase is a liquid crystal (LC) phase. Commonly, the droplets of LC emulsion are made by using thermotropic LC and an appropriate surfactant. Here the surfactant is playing an additional role in imposing strong anchoring boundary conditions for the nematic director inside droplets. The resulting effect is that there is an additional elastic energy contribution to the overall balance, which arises from topological defects in the confined nematic. This energy creates a significant barrier for droplet coalescence and leads to a new effect-topological stability of emulsions.^{4,7}

Droplets of nematic LCs in an isotropic fluid, as well as the related topological defect structures, have been extensively studied before. One of the earliest significant contributions to this field is by Volovik and Lavrentovich.8 Much work has been done in this field in the context of polymer-dispersed LCs.⁹ However, in most cases, the properties and effects of individual droplets have been addressed. Interesting physical effects here stem from the topological constraint, imposed on the director field in a closed volume by the anchoring condition on its surface,⁸ leading to topological defects of total point charge (+1) for a nematic and more complex structures in other phases. Topological defects in nematic drops, composed by archetypical thermotropic nematic LCs, such as 5CB or E7, depending of boundary conditions, are described in an extensive literature.^{8,10-12} Topological defects in cholesteric LC drops were studied as well, giving the influence of the boundary conditions on the negative-positive monopole transition.^{10,13} A recent paper investigates the effects of surfactant structure on the orientation of thermotropic nematic LC (5CB) specifically at aqueous interfaces.¹⁴

It has been demonstrated that some director singularities inside nematic droplets lead to the effect of topological stability against droplet coalescence, which is controlled by the balance of Frank

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Figure 1. A group of tightly squeezed nematic droplets of nematic E7 in water matrix with SDS surfactant (see Section 3). Image (a) shows the classical Maltese cross signature of a (+1) topological defect in the droplet center, viewed between crossed polarizers. Image (b), obtained with a more sophisticated technique of monitoring the phase contrast, reveals the radial director distribution. Here φ is the azimuthal angle of the director in the image plane varying between 0° and 180° according to the color scheme. 550 nm refers to the light wavelength used, and the black bar represents a 8 μ m length scale.



Figure 2. (a) Sketch of topological defect balance on the attempted droplet coalescence; (b) small droplets which are not topologically charged (WR/K \ll 1) should coalesce freely.

elasticity and the anchoring energy of the confined LC.^{4,7} Studies of collective properties and aggregation of nematic droplets in an isotropic suspending matrix (usually water)^{4,12} clearly demonstrated that the droplet coalescence is significantly hindered in the nematic phase. However, if the droplets are heated above the nematic—isotropic transition, the coalescence of the whole sample occurs within a few seconds. This indicates that the surfactant coverage is not the dominant factor responsible for droplet stability: the nematic ordering inside the droplets is the key factor, providing the barrier for coalescence.

Figure 1 illustrates the point. Each nematic droplet of E7 contains a topological point charge of (+1); the sketch in Figure 2 gives an example of a radial monopole that results from the perpendicular (homeotropic) anchoring at the boundary. If two droplets attempt to join, the resulting single simply connected bounded nematic volume must have just one (+1) point defect, according to the basic topological rules.¹⁵ Unless one invokes

some unlikely long-range interaction that brings both (+1) defects in each droplet to the point of contact at exactly the right moment of time, allowing them to simultaneously undergo the required transformations, we have to assume that these two defects remain initially unaffected by the droplets merging. Hence, in between, another defect with point charge (-1) must be born and then annihilated with one of the two initial (+1) monopoles. This defect could be, as one can see from the Figure 2a, a ring of the wedge disclination with the linear charge (-1/2) on the tip of the neck connecting the two droplets.

There is more than one late-stage scenario for this pair coalescence. One possibility is that the ring detaches itself from the surface, when the curvature of the neck decreases, transforming into a hyperbolic monopole structure with point charge (-1)which then drifts into the volume toward one of the radial monopoles. The other is that the (-1/2) ring remains as a surface disclination and one of the point defects moves toward it and disappears on the surface. This choice is curious but is of little relevance to the encapsulation phenomenon: what is important is that in order to form the initial neck the system must create an accompanying total (-1) point charge in isolation, at a distance $\sim R$ (the droplet radius) from other defects. This costs a macroscopic elastic energy $\Delta \approx KR$ (with K the characteristic value of Frank elastic constant), while the gain due to the surface tension is minimal as the total area of the "dumb-bell" is initially the same as of the two separate droplets. The elastic energy barrier for droplet coalescence, Δ , is proportional to the square of the nematic order parameter Q, via $K \propto Q^2$ in the leading order, and disappears in the isotropic phase.

The other important factor in this argument is the overall topological state of nematic droplets. The singularities of nematic director field only arise when the anchoring on the droplet surface is strong enough, so that the system "prefers" to pay an elastic energy for the topological defect instead of violating the boundary conditions. The director anchoring energy, W, is a small anisotropic correction to the main surface tension. Like the Frank elastic constant, it disappears in the isotropic phase; however, in the leading order, it is proportional to the linear power of nematic order parameter, $W \propto Q$. The characteristic dimensionless parameter WR/K controls the state of the emulsion. Small droplets should coalesce until the topologically charged regime $WR/K \ge 1$ is reached corresponding to a critical radius R^* ($R \ge R^*$).

Compared to thermotropic LC phases, the lyotropic LCs have not attracted the same attention and their practical significance is often underestimated. However, an analogous W/O emulsion based on lyotropic LCs could present a great interest in industrial applications because lyotropic systems are generally less toxic or not toxic compared to thermotropic LCs. The influence of lyotropic LC order on emulsion properties is investigated in this work by studying emulsions where the droplets are made of lyotropic cholesteric phase of cellulose. In this work, we do not study the initial dynamics of coalescence, when the liquid crystalline emulsion becomes gradually depleted of droplets with $R < R^*$ (see, e.g., ref 7). Our aim is to examine the fully aged emulsions and confirm the effect of spontaneous size selection of the droplets depending on a critical radius R^* . We use two different (although related) techniques to determine the droplets size in the sub-micrometer range: the classical dynamic light scattering (DLS) and the commercial nanoparticle characterization system Nanosight Halo LM10. Similarity of their results supports our conclusions about topological stabilization and the spontaneous size selection.

In the next section, we briefly describe the materials used and preparation protocols used to make the emulsions of water-based

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Figure 3. Chemical structures of (a) SDS (sodium dodecyl sulfate) with a molecular mass M = 288 g/mol and a HLB value of 40.0; and (b) of Zephrym PD2206 with a HLB value of 2.3.

lyotropic LCs dispersed in oil (cholesteric, W/O), and of the thermotropic LC dispersed in water (the latter, nematic O/W system, is better studied and is used as a reference). Following that, in Section 3, we describe the DLS method of determining the emulsion size distribution. This is done in some detail, discussing the strong aspects of this analysis and its challenges and ambiguities. Section 4 presents the results of a size distribution study performed with the Nanosight device; this section is necessarily short since we have less control over the analysis. Finally, in Conclusions, we compare the results on the two types of emulsions and discuss to what degree do they match the theoretical expectations.

2. Experimental Section

2.1. Surfactants. Surfactant is essential in order to impose strong boundary conditions on the nematic director and to stabilize the emulsions against coalescence. For the classical thermotropic nematic emulsion of E7/water, the boundary conditions can be created by using SDS (sodium dodecyl sulfate) surfactant with a molecular mass M = 288 g/mol and a HLB value of 40.0 from Acros Organics. For our new lyotropic hydroxypropyl cellulose (HPC) emulsion, the surfactant hydrophilic head must possess an affinity with both water and HPC, which is the composition of the dispersed phase. At the same time, the surfactant has to be perfectly soluble in the continuous phase (oil). After several materials were tried, the Zephrym PD2206 surfactant from Uniqema was used (see Figure 3).

2.2. Thermotropic E7 Emulsion. The classical nematic O/W emulsion is made of water with surfactant as the continuous phase, with the thermotropic nematic LC as the dispersed phase. Here we use the E7 material (from Merck), which is essentially a mixture of cyanobiphenyl mesogenic compounds with 5CB in the majority. E7 is one of the most commonly used nematic LCs with a broad range of nematic and no additional mesophases. The nematic-to-isotropic transition of E7 is $T_{\rm NI} \approx 58$ °C. The emulsion was prepared at 4 × CMC value of SDS (CMC_(SDS) = 0.236 g/L¹⁹) using deionized water. After addition of the E7 to water containing surfactant, the macroscopically phase-separated system was emulsified using a Cole–Parmer ultrasonic processor without particular precautions to get monodisperse emulsion.

2.3. Lyotropic HPC Emulsion. We used HPC in water as an aqueous lyotropic LC phase for making W/O emulsions. The HPC was obtained from Sigma–Aldrich with a number average molecular weight $M_n = 10\ 000\ \text{g/mol}$ and a weight average molecular weight $M_w = 80\ 000\ \text{g/mol}$. The chemical structure of HPC is given in Figure 4.

The solution of HPC in water is a lyotropic LC between 60 and 80 wt% HPC at room temperature. It has the cholesteric phase according to the phase diagram (Figure 5).²⁰⁻²² At room temperature and between 60% and 70% of HPC weight fraction, the LC phase presents several colors due to the selective reflection varying with



Figure 4. Chemical formula of hydroxypropyl cellulose with $M_n = 10\ 000\ \text{g/mol}$ and $M_w = 80\ 000\ \text{g/mol}$.



Figure 5. Phase diagram of hydroxypropyl cellulose–water, as given by R. S. Werbowyj and D. G. Gray.²²

the cholesteric pitch length. 22 This last is depending of two parameters: the temperature and mainly the HPC weight fraction.

The emulsion was obtained by mixing the lyotropic LC (l-LC) with the oil containing the surfactant. In a first step, the l-LC phase, composed of 60 wt% HPC and 40 wt% water (Figure 5) was prepared. In a second step, a certain amount of surfactant (Span 80 or Zephrym PD2206) was added to the oil at a concentration of 1 wt%. In this work, we choose heptane as the continuous oil phase due to its low viscosity, $\eta = 0.41$ mPa·s at T = 293 K, required to increase the Brownian mobility of the droplets in DLS experiments. At the last step of preparation, the l-LC and the oil containing surfactant were mixed together with a high-shear-rate mixer, Silverson L4R. After being mixed, the obtained emulsion was filtered with a Millipore membrane filters Fluoropore FS, pore size $3 \mu m$, to eliminate the excess of the l-LC, which was not emulsified. We shall see from the results that this filtration had no or little effect on the vast majority of small droplets around the critical topological size, R^* . The mixing and the filtration produced a unquantified loss of the l-LC; however, a more concentrated emulsion can always be obtained by sedimentation of the dispersed phase and removing the excess of heptane.

3. Dynamic Light Scattering

3.1. Size Distribution Analysis. DLS is a powerful technique for characterizing the droplet size distribution of a dilute emulsion. DLS measurements involve the analysis of the autocorrelation function of scattered light, obtained from a digital correlator at a specific scattering angle, as a function of time.^{16,17} The normalized autocorrelation function of the intensity of the scattered light, $g_2(t)$, for a given delay time, τ , is the raw experimental output. It can be expressed as a function of the field autocorrelation function, $g_1(t)$,^{17,18} by $g_2(t) = B(1+\beta|g_1(t)|^2)$. The factor *B* is the baseline corresponding to the long-time tail value of the measured $g_2(t)$. This is an important and often ambiguous factor in the DLS analysis. The parameter β is the coherence factor, which is generally considered as an adjustable parameter in the data analysis. If the system under investigation has only one decay process, which corresponds to a distribution

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of monodisperse particles in solution, then the field autocorrelation function, $g_1(t)$, decays exponentially:¹⁶

$$g_1(t) = \exp(-\Gamma t); \text{ or } g_2(t) = B(1 + \beta \exp(-2\Gamma t))$$
 (1)

The latter relation is used as the fitting function to provide the parameter of interest, Γ , the inverse of the relaxation time, $\tau =$ $1/\Gamma$. This can be done in two different ways, depending on whether the value of the baseline B is reliably known or not. The linear method (with fixed B) has the disadvantage that, for values of $g_2(t)$ close to B, corresponding to long times t, the scatter in the data is enhanced and significant uncertainty in the values of the fitted parameters is introduced. Naturally, this procedure is very sensitive to the correct value of B.¹⁶ The nonlinear method provides better results, at the expense of having the additional fitting parameter B, which may or may not end up close to the value expected from experimental considerations. An initial guess for the parameter Γ is introduced, and its value is corrected in successive iterations until the desired precision is reached. In this procedure, all the three parameters Γ , β , and B are determined by the fit, and no assumption is made about the baseline value.

For a polydisperse emulsion, $g_1(t)$ can no longer be represented as a single exponential and could be treated as a sum over a distribution of decay rates, $A(\Gamma)$. Treating this as the Laplace transformation procedure, we have

$$g_1(t) = \int_0^\infty A(\Gamma) \exp(-\Gamma t) \,\mathrm{d}\Gamma \tag{2}$$

with normalized distribution

$$\int_0^\infty A(\Gamma) \, \mathrm{d}\Gamma = 1 \tag{3}$$

The distribution function of decay rates, $A(\Gamma)$, can be a broad continuous distribution, a series of discrete δ functions, or some combination of the two.

There is a direct relationship between the inverse relaxation time, Γ , and the particle size. The diffusion coefficient of droplets in the matrix, *D*, is linked to the relaxation time, τ , by the Stokes–Einstein relation

$$D = \frac{k_{\rm B}T}{6\pi\eta R_{\rm h}} = \frac{\Gamma}{q^2} \equiv \frac{1}{q^2\tau}$$
(4)

where *q* is the magnitude of the scattering wave vector, $q = (4\pi n/\lambda_0) \sin(\theta/2)$, related to the scattering angle, θ , wavelength of incident light, and the average refractive index of the medium. This provides the measure of droplet hydrodynamic radius, R_h , from the given value of relaxation rate: $\Gamma = (q^2 k_B T/6\pi \eta)[1/R_h]$. Therefore, one can straightforwardly transform the distribution $A(\Gamma) d\Gamma$ into the required $A(R_h) dR_h$, which is plotted as our main result.

The analysis of experimentally provided data for $g_2(t)$ in our case follows the routine of first finding the $g_1(t)$ and then inverting the Laplace transformation, eq 2, to obtain the function $A(\Gamma)$.¹⁶ The numerical package GENDIST involves the REPES (regularized positive exponential sum) procedure for the inversion of Laplace transformation and a special fitting algorithm CONTIN that allows for adjusting the rejection probability of the outcome.

3.2. Droplet Size Distribution. The droplets size distribution was obtained by using DLS. The apparatus used for the DLS experiments was an ALV 5000E system equipped with a multibit and multi- τ Malvern correlator 4700c (256 channels). The light source was a laser Millenia II from Spectra-Physics with a wavelength $\lambda = 532$ nm and a power output of 2 W. The



Figure 6. Normalized correlation function, g_2 , at $\theta = 15^\circ$ of O/W emulsion composed by a thermotropic LC E7 droplet in a matrix of water/SDS. The fit function (solid line) obtained by Laplace-transform inversion routine outputs the distribution of relaxation times, $A(\Gamma)$. Inset: the residuals plot, indicating a very good fit with symmetric deviations even on the long-time tail.



Figure 7. Size distribution [normalized $A(R_h)$] of O/W emulsion composed of thermotropic LC E7 droplets in a matrix of water/SDS. The average hydrodynamic radius is 450 nm.

measurements of the scattered light were realized at a fixed angle, θ , from the transmitted beam and at a fixed temperature of T = 20 °C.

The classical O/W emulsion [E7/(water/SDS)] was not filtered at any stage. We choose a low angle, $\theta = 15^{\circ}$, in order to reach a sufficiently high inverse scattering vector, q^{-1} , so that only the diffusional process is contributing to the total intensity and not the internal mode dynamics.¹⁶ Moreover, we have observed almost no q dependence of intensity at higher scattering angles, θ , up to 50°, which means that the emulsion is monodisperse enough. To avoid multiple scattering, the sample was strongly diluted until the intensity of scattering became linearly proportional to the remaining emulsion concentration. After measuring the normalized correlation function, $g_2(t)$, at a fixed scattering angle, we fitted it by using the REPES routine. The result of fitting, presented in Figure 6 appears quite satisfactory.

This fit allows us to get size distribution $A(\Gamma)$, which is then transformed into the required normalized distribution of particle sizes, $A(R_h)$. The plot in Figure 7 indicates a relatively narrow distribution with an average hydrodynamic radius, $R_h = 450$ nm. We would like to emphasize that no artificial size selection was undertaken in this E7 O/W emulsion. Although it is important that we do not have any noticeable population of large droplets (despite long time allowed for the emulsion to age), the key result is that there are no droplets observed with the size smaller



Figure 8. Normalized correlation function, g_2 , at $\theta = 30^\circ$ of W/O emulsion composed by lyotropic LC (HPC/water) droplet in a matrix of heptane/Zephrym PD2206. The fit function is shown by the solid line. Inset: the residuals plot, indicating a very good fit except at the very long-time tail of $g_2(t)$ where the deviations become slightly nonsymmetric.



Figure 9. Size distribution [normalized $A(R_h)$] of W/O emulsion composed by lyotropic LC (HPC/water) droplet in a matrix of heptane/ Zephrym PD2206. The average hydrodynamic radius given by REPES routine is $R_h = 310$ nm.

than ~ 200 nm. Since initial emulsification provides droplets of much smaller sizes, this observation means that small droplets have all coalesced but the process has stopped on reaching a size of 200 nm. We identify this size with the critical topological size $R^* = K/W$ for this type of LC and interface. The topological defect inside the droplets above R^* prevents further coalescence.

The W/O emulsion [(HPC/water)/(Heptane/Zephrym PD2206)] was filtered with a pore diameter of 0.7 μ m in order to access only to the diffusional motion of the droplets and not to the internal mode dynamics. Indeed, if some droplets are too large (more than 1 μ m), we will obtain information about the internal dynamics as well and it will contribute with the diffusional process to the total intensity.¹⁶ No *q* dependence of the total intensity was observed, which means we accessed only the diffusional process contribution. Again, the sample was diluted until the linear intensity—concentration regime was reached so that we were assured of the absence of multiple scattering. After measuring the normalized correlation function $g_2(t)$ at a fixed angle, $\theta = 30^\circ$, we fitted it by using the same analytical routine (see Figure 8).

The droplet size distribution $A(R_h)$, obtained as the output of this fitting and the subsequent transformation from $A(\Gamma)$, is plotted in Figure 9. The average hydrodynamic radius, $R_h = 310$ nm, was slightly under the filter pore radius ($R_f = 350$ nm).

As previously, there were apparently no droplets with the size below the critical radius, $R^* \approx 180$ nm. Therefore, we again



Figure 10. Size distribution of polystyrene latex particles in water, with the maximum at a radius R = 170 nm.



Figure 11. Size distribution of the O/W emulsion of E7 in water.

observed a self-selection of the droplet size due to the creation of a topological defect inside the droplets as soon as a characteristic size is exceeded.

4. Nanoparticle Detection

The Halo LM10 nanoparticle detection system from Nanosight is a standalone device for particle sizing. The technique combines the optical microscopy image analysis with light scattering data analysis to cover the broad range of possible sizes in one detection pass. The emulsion sample is introduced into the flow cell with a syringe, and the focus of the microscope is adjusted in order to visualize the particles directly. The images are captured with a CCD camera and analyzed with an image analysis program providing the size distribution in the optical resolution range, while the independent monochromatic scattering at large angles provides the count of smaller droplets. To test the quality of size distribution analysis provided by this device, we have first analyzed a sample of monodisperse polystyrene latex particles of radius R = 150 nm in water, obtained from Sigma–Aldrich. The size distribution produced by the Nanosight equipment is shown in Figure 10. It confirms the expected narrow distribution, with the peak slightly spread and centered on a radius R = 170nm. This result is in good agreement with the particle size analysis given by the manufacturer.

Next, we characterize the size distribution of a thermotropic O/W emulsion E7/(water/SDS) to compare it with the results provided previously by the DLS. The result is presented in Figure 11 and again suggests a reasonably monodisperse distribution. The maximum is centered on a radius size of R = 500 nm, which is in excellent agreement with the direct light scattering results. We note that there are no droplets detected of radius smaller than



Figure 12. Size distribution of the W/O emulsion of HPC in heptane.

250 nm. Considering an inevitably high error, we conclude that the critical topological radius of this emulsion is $R^* \approx 200$ nm. The result for size distribution of the new lyotropic liquid crystalline W/O emulsion is shown in Figure 12. This distribution also confirms a narrowly peaked population of droplets centered on a radius size $R \approx 300$ nm and with a critical topological radius

value $R^* \approx 170$ nm, below which there are no smaller droplets detected by either of the two methods.

5. Conclusion

We have studied the stability and the self-selection of droplet size in two types of liquid crystalline emulsion: one classical thermotropic O/W emulsion of a thermotropic nematic LC dispersed in water, the other a new lyotropic liquid crystalline phase of hydroxy propyl cellulose dispersed in a low-viscosity oil (heptane).

In each case, we chose an appropriate surfactant in order to stabilize the emulsion respectively but mainly to impose specific boundaries conditions at the oil-water interface. The SDS surfactant creates a perpendicular anchoring of the E7 nematic LC, which leads to a radial monopole topological defect droplet conformation. The Zephrym PD2206 surfactant creates a tangential anchoring of cholesteric lyotropic LC in our new W/O cholesteric emulsions, which leads to concentric shells of director with a topological point defect at the center. Both conformations possess a topological charge (+1), required for the simply connected droplet volume, and appear to confirm the presence of an elastic energy barrier against coalescence.

Since the key length scale of such systems, the topological radius $R^* = K/W$, is expected to be in the range of a few hundred nanometers, the optimum technique to determine the size distribution is light scattering. Our findings suggest that both emulsions have adopted a relatively narrow monomodal distribution (with an average size of 450 nm for the E7 O/W and 310 nm for the HPC W/O emulsion, respectively). The main result is that we detect no droplets below a certain size, which agrees with the concept of a critical radius, R^* . It is, in some way, remarkable that the concepts of curvature (Frank) elasticity of LC have such a profound effect on a lyotropic system, where we know the Frank elastic constant, K, is much lower than in thermotropic nematic LCs. The similarity of length scales resulting from the K/W balance in the two systems is quite surprising. These results can be used as a new approach to obtain stabilized and narrowly distributed emulsions, using the elasticity of the liquid crystalline mean field inside the droplets.

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