

Shear Rupturing of Complex Fluids: Application to the Preparation of Quasi-Monodisperse Water-in-Oil-in-Water Double Emulsions

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Quasi-monodisperse emulsions can be obtained by shearing a crude polydisperse one within a very narrow gap (*Langmuir* **1997**, 4600–4613). In this paper, we apply the emulsifying technique developed for simple emulsions to fabricate double emulsions of controlled size. We first prepare quasi-monodisperse and concentrated water-in-oil emulsions using a Couette mixer. This inverted emulsion is emulsified in an aqueous phase using the same apparatus. We obtain water-in-oil-in-water double emulsions made of oily globules containing smaller water droplets, both colloids having well-defined and controlled diameter.

I. Introduction

The rupturing of an isolated droplet of one viscous fluid in another immiscible fluid is a classic problem in fluid mechanics with special relevance in the field of emulsification. The way in which the shear stresses induced by the flow overcome the interfacial tension between the two fluids to finally rupture the droplet has been addressed in increasing levels of detail^{1–8} since the pioneering work of Taylor.⁹ Recently, an efficient technique for producing quasi-monodisperse emulsions has been developed.^{10–12} It consists of shearing a premixed emulsion made of large polydisperse droplets. Following the work of Mason et al.,^{10,11} Mabillet et al.^{12,13} found out experimentally that two conditions have to be fulfilled to get monodispersity: (1) the gap of the shear cell has to be as narrow as possible (of the order of 100 μm or less) and (2) the viscosity ratio between the dispersed and continuous phases has to be close to unity. On the basis of these observations, a Couette cell has been built for the rapid production of simple emulsions of controlled diameter.^{10–13} Recent studies¹³ reveal that the fragmentation of a polydisperse emulsion leads very rapidly (less than 1 s) to a monodisperse one when the shear stress is strong enough and when the initial size of the droplets is much larger than the final one. The drops of the initial emulsion deform into thin liquid threads of the same radius. Below some critical

radius, the threads disrupt into several small droplets of the same size via the development of a capillary instability. When the shear stress is lower or when the initial size is close to the final one, drops break into few droplets (typically two or three droplets). Fragmentation in this latter case obeys much lower kinetics (many hundred seconds). Whatever the kinetics, the final droplet size is independent of the initial polydispersity and of the rheological behavior of the material, being essentially dependent upon the applied viscous stress.

The study of the effect of shear on the fragmentation of oily globules to produce water-in-oil-in-water (W/O/W) polydisperse emulsions has been developed in recent publications.^{14,15} The goal of this paper is to demonstrate that the method that has been developed for simple emulsions can be extended to produce quasi-monodisperse double emulsions, within the same rheological and shearing conditions. We first prepare quasi-monodisperse and concentrated W/O emulsions using a Couette mixer. This inverted emulsion is emulsified in an aqueous phase using the same apparatus. We obtain W/O/W double emulsions made of oily globules containing smaller water droplets, both colloids having a well-defined and controlled diameter.

The remainder of this paper is organized as follows. A short theory section reviews the shear rupturing of droplets of one viscous fluid in another immiscible one. An Experimental Section describes our sample preparation, shearing methods, characterization, and observation techniques. This is followed by our experimental results of the droplet size as a function of emulsion composition and shearing conditions.

II. Theory

1. Rupturing of Isolated Droplets. We first consider the rupturing of a single droplet of viscosity η_d , suspended in a fluid having viscosity of η_c at low Reynold's number.⁸ The continuous phase is submitted to a shear rate of $\dot{\gamma}$. For droplet deformation to occur, the viscous shear stress

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(1) Bartok, W.; Mason, S. G. *J. Colloid Sci.* **1959**, *14*, 13.

(2) Chandrasekhar, S. *Hydrodynamic and Hydromagnetic Stability*; Oxford: London, 1961.

(3) Grace, H. P. *Chem. Eng. Commun.* **1982**, *14*, 225.

(4) Hinch, E. J.; Acrivos, A. *J. Fluid Mech.* **1980**, *98*, 305.

(5) Khakar, D. V.; Ottino, J. M. *Int. J. Multiphase Flow* **1987**, *13*, 71.

(6) Mikami, T.; Cox, R. G.; Mason, S. G. *Int. J. Multiphase Flow* **1975**, *2*, 113.

(7) Rumscheidt, F. D.; Mason, S. G. *J. Colloid Sci.* **1961**, *16*, 238.

(8) Rallison, J. M. *Annu. Rev. Fluid Mech.* **1984**, *16*, 45.

(9) Taylor, G. I. *Proc. R. Soc. London, Ser. A* **1934**, *146*, 501.

(10) Mason, T. G.; Bibette, J. *Phys. Rev. Lett.* **1996**, *77*, 3481.

(11) Mason, T. G.; Bibette, J. *Langmuir* **1997**, *13*, 4600.

(12) Mabillet, C.; Schmitt, V.; Gorria, Ph.; Leal-Calderon, F.; Faye, V.; Deminière, B.; Bibette, J. *Langmuir* **2000**, *16*, 422.

(13) Mabillet, C. Fragmentation in Emulsions Submitted to a Simple Shear. Ph.D. Thesis, University Bordeaux 1, 2000.

(14) Muguet, V.; Seiller, M.; Barrat, G.; Ozer, O.; Marty, J. P.; Grossiord, J. L. *J. Controlled Release* **2001**, *70*, 37.

(15) Muguet, V.; Seiller, M.; Barrat, G.; Clausse, D.; Marty, J. P.; Grossiord, J. L. *J. Colloid Interface Sci.* **1999**, *218*, 335.

of the continuous phase, $\eta_c \dot{\gamma}$, must overcome the characteristic Laplace pressure, σ/R , where R is the droplet radius and σ the oil–water interfacial tension. For rupturing to occur, the capillary number, $Ca = \eta_c \dot{\gamma} R / \sigma$, defined as the ratio of the shear stress to the Laplace pressure, must exceed a critical value of Ca_c . This implies that the droplet has been elongated by the viscous shear before rupturing. The average radius of the ruptured droplets is therefore given by

$$R \approx Ca_c \frac{\sigma}{\eta_c \dot{\gamma}} \quad (1)$$

This scaling form had been originally derived by Taylor.⁹ A complete description of the deformation and bursting of isolated droplets under shear is complicated since the critical capillary number Ca_c depends on the viscosity ratio η_d/η_c and the type and history of the shear flow.⁸ Experiments have identified different rupturing scenarios that may occur when the shear is increased very gradually (quasi-static conditions).^{1,2,5,6} Very recently, Mabillet et al.¹³ have explored the rupturing of isolated droplets in conditions where rapid transients in the shear rate are applied. Their experimental work focuses on fragmentation in simple shear flow conditions. The main results can be summarized as follows:

(i) For $Ca \gg Ca_c$, the droplet is stretched into extremely elongated threads that undergo a capillary instability and breaks into a chain of many droplets. Such an elongated droplet resembles a liquid cylinder that is susceptible to a capillary instability in which the surface tension drives the rupturing of the cylinder into many droplets having less total surface area. The characteristic time for deformation and rupturing generally does not exceed 1 s. In this regime, the critical capillary number is minimum for $0.1 < (\eta_d/\eta_c) < 1$ and is of the order of 0.2. The radius of the elongated threads before rupturing is independent of the initial droplet size and this is the reason the final emulsion is quasi-monodisperse.

(ii) For $Ca \geq Ca_c$, i.e., when the initial droplet size is very close to the final one, the droplet is ruptured into two or three droplets of almost equal volume. The characteristic time is much longer, being of the order of many hundred seconds.

(iii) The final droplet size is independent of the initial polydispersity, the flow history, and the rheological behavior of the emulsion. It essentially depends on the applied viscous stress.

2. Rupturing of Interacting Droplets. The existing attempts to understand the influence of the emulsion's droplet volume fraction, ϕ , on droplet rupturing have treated the emulsion as an effective medium, thereby ignoring the precise microscopic dynamics accompanying the rupturing.^{10,11,16} The ruptured droplet size in emulsions has been proposed to follow eq 1 with an elevated effective viscosity η_{eff} , which reflects the role of ϕ :

$$R \approx Ca_c \frac{\sigma}{\eta_{\text{eff}} \dot{\gamma}} \quad (2)$$

According to this relation, the overall viscosity of the emulsion, and not that of the continuous phase alone, determines the average final size of the ruptured droplets. For a compressed emulsion at high ϕ , η_{eff} can be many times η_c , so the ruptured droplet sizes can be much smaller than eq 1 would predict.

III. Experimental Section

The measurements of the interfacial tension were performed on a Krüss tensiometer (site 04), using the spinning drop technique. The measurements were performed at the oil–water interface. Both water and oil phases contained the same hydrophilic and lipophilic surfactants as the ones used for double emulsion fabrication. The measurements were performed at room temperature of 22 °C. The measurements of the viscosities were carried out on a controlled strain and stress rheometer, CarriMed 500, equipped with different cone-plane measuring tools.

1. Couette Cell Description. A Couette mixer consisting of two concentric cylinders was used for emulsion fabrication. A scheme of the setup is available in ref 12. The inner cylinder of radius $r \approx 20$ mm is moved by a motor that rotates at a selected angular velocity, ω , which can reach up to $71.2 \text{ rad} \cdot \text{s}^{-1}$. The outer cylinder is immobile, and the gap between the stator and the rotor is fixed at $e = 100 \text{ } \mu\text{m}$. For the maximum angular velocity, we are able to reach very high shear rates, $\dot{\gamma} \approx r\omega/e = 14\,200 \text{ s}^{-1}$, in simple shear flow conditions. A premixed crude emulsion is pushed into the gap between the rotor and the stator by means of a piston. The residence time of the emulsion inside the mixer gap is of the order of 10 s. Generally, the operative conditions are such that $Ca \gg Ca_c$, meaning that the initial droplet size is much larger than the final one. With this Couette mixer, it is possible to produce significant quantities of emulsions with very narrow size distribution (up to 1 L/h, depending on the system, at volume fractions ranging from 70 to 90%).

2. System Composition. W/O/W quasi-monodisperse emulsions are fabricated following a two-step procedure.¹⁷ We first prepare a quasi-monodisperse W/O inverted emulsion, stabilized by an oil soluble surfactant. Salt (NaCl) is added to the dispersed phase in order to avoid any rapid coarsening phenomenon.¹⁸ A double emulsion is fabricated by dispersing the inverted one within an aqueous continuous phase containing a hydrophilic surfactant. Large oil globules are produced, each one containing smaller inverted water droplets. Salt or glucose is added in the external water phase in order to avoid any osmotic pressure mismatch between the internal and the external water compartments. For the oil phase, we used either dodecane (from Aldrich) or commercial sunflower oil (Stora).

To stabilize inverted W/O emulsions, we used one of the following surfactants, each of them being oil soluble: Admul Wol 1403 (Polyrycinoleate of polyglycerol) from QUEST International, $M_w \approx 4400 \text{ g/mol}$, hydrophilic–lipophilic balance (HLB) = 4; Arlancel p135 (polyethylene-30 dipolyhydroxystearate) from ICI, $M_w \approx 5000 \text{ g/mol}$, HLB = 5–6; Arlancel 186 (glyceryl monooleate) from ICI, HLB = 3.

To stabilize direct O/W emulsions, we chose a hydrophilic surfactant: Synperonic PE/F 68 provided by ICI. This surfactant is a triblock copolymer of ethylene oxide (EO) and propylene oxide (PO). The average formula is 75 EO/30 PO/75 EO. The average molecular weight is $M_w \approx 8400 \text{ g/mol}$ and HLB = 29. In some experiments, to increase the viscosity of the external water phase, we added a polysaccharide, alginate HF120L, of molecular weight $M_w \approx 54\,000 \text{ g/mol}$, provided by Disatec from Promova. This polymer consists of D-mannuronate and L-gulonate. It acts as a thickening agent and has only weak interfacial properties since it does not vary the interfacial tension between oil and water in the presence of the previously mentioned surface agents. Moreover, alginate molecules do not stabilize emulsions by themselves, i.e., in the absence of surface-active species.

3. Premix Preparation. The first step consists of preparing a crude polydisperse emulsion, the so-called premixed emulsion. It is obtained by incorporating the dispersed phase with very gentle stirring in order to avoid the formation of small droplets. The preparation of the primary W/O premix is generally quite easy. However, special care has to be taken for the preparation of a concentrated double emulsion premix. In the latter case, the inverted emulsions are introduced into the water phase very gradually to avoid the formation of "multiple structures" like the one shown in Figure 1a. Indeed, when introduced rapidly in the

(17) Pays, K.; Leal Calderon, F.; Bibette, J. French Patent, CNRS, No. 99 11745.

(18) Aronson, M. P.; Petko, M. F. *J. Colloid Interface Sci.* **1993**, *159*, 134.

(16) Aronson, M. P. *Langmuir* **1989**, *5*, 494.

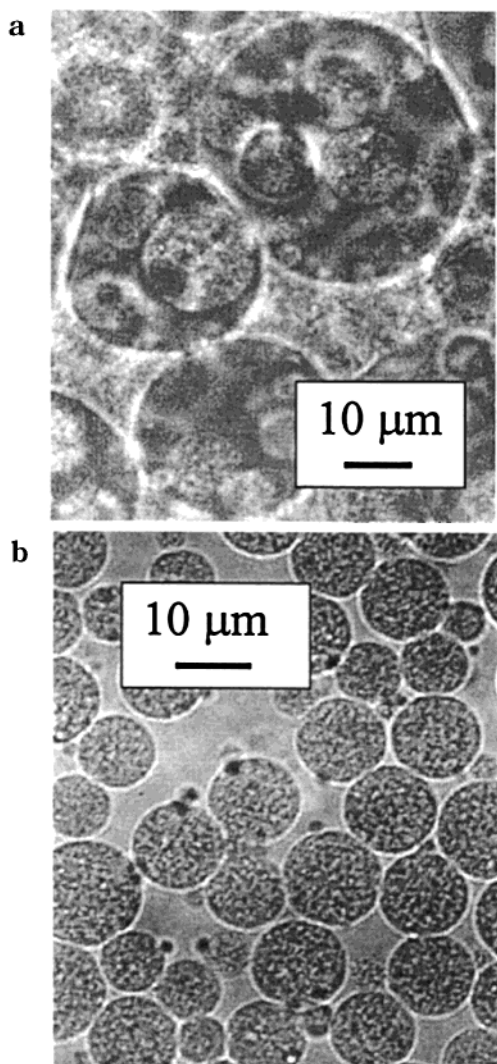


Figure 1. (a) Complex structures obtained when the incorporation of the primary inverted emulsion in the external water phase is too fast giving a W/O/W/O emulsion. (b) Microscopic image of a typical premixed W/O/W emulsion.

water phase, the inverted emulsion may incorporate water and very complex structures are then produced. In Figure 1a, we can observe W/O/W/O structures resulting from this process. Such structures, once formed, cannot be transformed to produce W/O/W double emulsions. Therefore, the inverted emulsion is introduced in the water phase at very low rate, i.e., drop by drop (around 0.5 cm³ every 5 s). In such conditions, the inverted emulsion is ruptured into double oil globules and does not incorporate water. In Figure 1b, we show a microscopic image of the premixed double emulsion successfully produced after taking all the previous necessary precautions. The droplets have sizes ranging from 10 to 20 μm.

4. Emulsion Characterization. The emulsions are observed with a phase contrast optic microscope (Zeiss, Axiovert ×100). Since the double emulsions possess a very narrow size distribution, it is easy to determine the average globule diameter from a simple microscopic image. We also used a Malvern Mastersizer granulometer to measure the size distribution of the emulsions. The collected scattered intensity as a function of the angle is transformed into the size distribution using the Mie theory. The mean droplet size in volume $D(4.3)$ is defined as:

$$D(4.3) = \frac{\sum_i N_i d_i^4}{\sum_i N_i d_i^3}$$

where N_i is the total number of droplets with diameter d_i . The polydispersity of the emulsion is characterized by a parameter termed as “uniformity” and defined as:

$$U = \frac{1}{\bar{d}} \frac{\sum_i N_i d_i^3 |\bar{d} - d_i|}{\sum_i N_i d_i^3}$$

where \bar{d} is median diameter, i.e., the diameter for which the cumulative undersized volume fraction is equal to 50%. In the following, we characterize the obtained emulsions through $D(4.3)$ and U . Here it is important to stress that in the special case of double emulsions, the scattering objects are optically nonuniform. Indeed, the double globules contain small water droplets with a characteristic size close to the wavelength of the laser beam (633 nm). The scattering properties of such complex objects are not considered in the software of our commercial granulometer. We therefore decided to use the Mie theory assuming that the double globules optically behave like simple droplets, with the same refractive index as the oil phase. This approximation, although questionable, revealed itself to be quite satisfactory. Indeed, for each sample, we checked that the average diameter $D(4.3)$ was very close to the one directly obtained from microscopic observations.

IV. Results

1. Inverted W/O Emulsion. The premixed emulsion is comprised of water droplets (NaCl, 0.2 M) dispersed in a 1:9 mixture (w/w) of dodecane and Admul wol 1403. The droplet mass fraction, ϕ_i , is set at 80%. This crude emulsion is sheared into the Couette cell at a constant shear rate of $\dot{\gamma} = 10\,000\text{ s}^{-1}$. We obtain a quasi-monodisperse W/O emulsion with an average diameter of 0.30 μm and uniformity, U , of the order of 20%. This primary emulsion will be employed for the preparation of all the double emulsions that will be considered below. To vary the droplet volume fraction, ϕ_i , the emulsion is diluted with pure dodecane after the fragmentation process.

2. Double Emulsions. A given amount of the primary inverted emulsion (mass fraction $\phi_g = 70\%$) is dispersed in an aqueous phase containing 5% (w/w) of Synperonic PE/F 68 as the hydrophilic surfactant and 0.4 M of glucose to match the osmotic pressure of the water droplets. In the absence of any thickening agent, the viscosity of the continuous phase is very low compared to that of the inverted emulsion. According to the experimental work of Mabillet et al.,¹³ quasi-monodisperse fragmentation occurs preferentially when the viscosity ratio between the dispersed phase and the continuous phase lies between 0.1 and 1. Therefore, we dissolve 2% (w/w) of alginate in water to increase the viscosity of the continuous phase. Due to its high molecular mass, alginate does not perturb the osmotic equilibrium between the internal droplets and the external water phase. Table 1 summarizes the compositions of the primary and double emulsions. To predict the best conditions to obtain quasi-monodisperse fragmentation, we plot in Figure 2 the evolution of the water phase viscosity η_c as a function of the shear rate and alginate concentration. For comparison, the viscosity η_d of the inverted emulsion at $\phi_i = 75\%$ (w/w) is reported in the same graph (up to 1000 s^{-1}). For a 2% (w/w) alginate solution, the viscosity ratio η_d/η_c is of the order of 1 at 1000 s^{-1} , so we can expect to obtain double globules with narrow size distribution in this alginate composition range. From the measured values of σ ($\sigma \approx 2\text{ mN/m}$ at the water/oil interface), eq 1 predicts that the droplet size must be close to 1 μm when the shear rate, $\dot{\gamma}$, is of the order of 10^4 s^{-1} ($\eta_c = 0.05\text{ Pa}\cdot\text{s}$, $\text{Ca}_c = 0.2$). Of course, the viscosity ratio becomes smaller than 1 in the presence of concen-

Table 1. Composition (% (w/w)) of Multiple Emulsions

	system: Admul wol/ Synperonic/dodecane	ratio	ratio	ratio	system: Arlcel p135/ Synperonic/sunflower oil	ratio
primary W/O emulsion	water + 0.2 M NaCl		ϕ_i		water + 0.4 M NaCl	40
	where ϕ_i equals	55	65	75	Arlcel P 135	3
	Admul wol 1403	12.5	14.8	17	sunflower oil	57
	dodecane	32.5	20.2	8		
external water phase	water + 0.4 M glucose	93			water + 0.8 M glucose	93
	Alginate HF 120L	2			Alginate HF 120L	2
	Synperonic PE/F 68	5			Synperonic PE/F 68	3
W/O/W double emulsion	W/O emulsion	70			W/O emulsion	60
	external water phase	30			external water phase	40

trated double globules, surfactant, and glucose since the whole emulsion viscosity, η_{eff} , should be considered instead of η_c ($\eta_{\text{eff}} > \eta_c$). However, we observed that the ratio remained in the adequate range, i.e., between 0.1 and 1, over the whole set of experiments.

The premixed double emulsion is sheared in the Couette cell at different shear rates from 0 to 14 200 s^{-1} . The obtained double emulsions have diameters ranging from 7 to 2 μm and uniformity between 15 and 30%. Figure 3 is a microscopic image of double emulsions fabricated at different shear rates. Large oil globules that are very uniform in size are visible, and the smaller inverted water

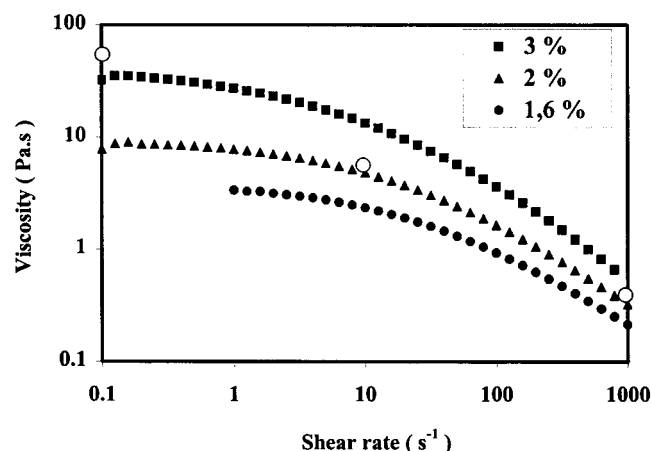


Figure 2. Evolution of the water phase viscosity η_c as a function of the shear rate and alginate concentration (filled symbols). For comparison, the viscosity, η_d , of the inverted emulsion at $\phi_i = 75\%$ (see Table 1) is reported in the same graph (open symbols).

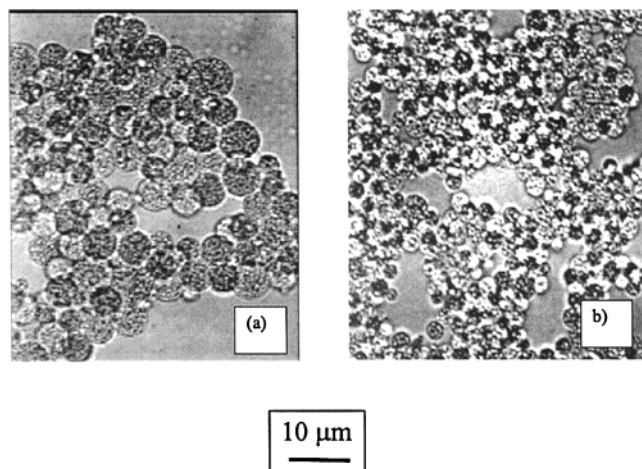


Figure 3. Image of the W/O/W emulsions obtained for the system: Admul wol 1403/Synperonic PE/F 68/dodecane. The composition is given in Table 1. $\phi_i = 65\%$. The emulsions were diluted with water and glucose to facilitate the observation. (a) $\dot{\gamma} = 1000 \text{ s}^{-1}$ and (b) $\dot{\gamma} = 14\,200 \text{ s}^{-1}$.

droplets are also distinguishable. From these results, it can be concluded that the fragmentation method that has been developed for simple emulsions can be extended to produce quasi-monodisperse double emulsions. In other words, the capillary instability occurring in simple emulsions also takes place in the presence of materials such as concentrated emulsions, within the same rheological and shearing conditions. It is worth noting that in our experiments the final globule size is always significantly larger than the internal water droplet diameter (there is at least a factor of 10 between the two diameters). In such conditions, the W/O emulsion may be considered as an effective continuous medium obeying the same fragmentation properties as a simple fluid.

a. Influence of the Internal Droplet Mass Fraction.

The primary W/O emulsion is diluted with dodecane to vary the mass fraction, ϕ_i , of the water droplets in the inverted emulsion. In Figure 4, we plot the evolution of the globule diameter as a function of $\dot{\gamma}$, for three different mass fractions ϕ_i . The mass fraction, ϕ_g , of the globules in the double emulsion is always equal to 70%. It can be observed that for a given shear rate, the globule size increases with the droplet mass fraction. When ϕ_i is varied, the average viscosity of the inverted emulsion also changes. Our results are qualitatively identical to the ones obtained by Mason et al.^{10,11} for the fragmentation of simple emulsions. Identically, they observed that when the viscosity of the dispersed phase is increased the droplet diameter also increases.

b. Influence of the Continuous Phase Viscosity.

The viscosity of the external water phase is varied by changing the alginate concentration. In Figure 5, we plot the $D(4.3)$ vs $\dot{\gamma}$ curve for two different alginate concentrations: 2% (w/w) and 3% (w/w). In this series of experiments, the viscosity, η_d , of the primary W/O emulsion is kept constant while the continuous phase viscosity, η_c , is varied. As in the previous set of experiments, the globule size increases with the ratio η_d/η_{eff} . However, the main explanation for this effect has to be attributed to the

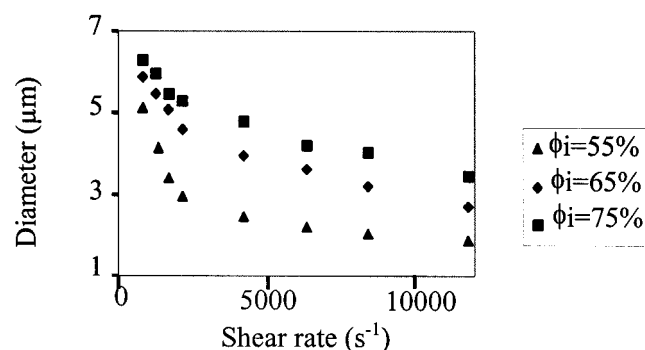


Figure 4. Dependence of the globule diameter in W/O/W emulsions on the steady shear rate, $\dot{\gamma}$, for the system: Admul wol 1403/Synperonic PE/F 68/dodecane. See Table 1 for detailed composition.

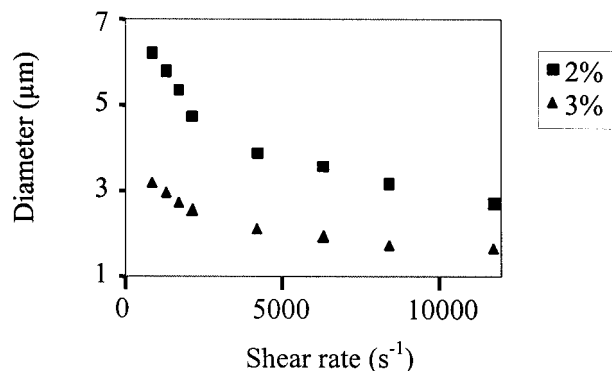


Figure 5. Influence of the external water phase viscosity on the globule diameter vs shear rate curves for the system: Admul wol 1403/Synperonic PE/F 68/dodecane. See Table 1 for the exact composition.

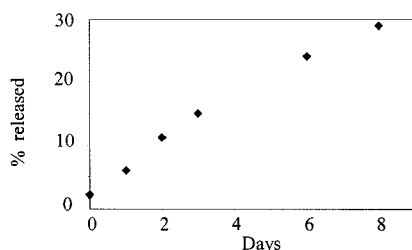


Figure 6. Rate of release of electrolyte from inner drops in double emulsions with an average globule diameter of 2.1 μm . System: Admul wol 1403/Synperonic PE/F 68/dodecane. The exact composition is given in Table 1. $\phi_i = 65\%$.

increase in the shear stress; at constant shear rate, $\dot{\gamma}$, the viscous stress in the presence of 3% (w/w) of alginate is larger and thus, according eq 2, the globule radius becomes smaller.

3. Kinetic Evolution. We used different techniques to study the kinetic evolution of the double emulsions. The concentration of salt (NaCl) present in the aqueous external phase is measured by means of an Ag/AgCl specific electrode which is sensitive to the chemical activity of chloride ions. The measured potential is transformed into salt concentration using a calibration curve. We combined this technique with direct observations under a microscope. It can be stressed that the entrapment yield right after the preparation step is rather elevated; indeed, we obtained at least 95% of the salt initially encapsulated, whatever the globule diameter was. This result can be regarded as a general feature of the fabrication method. For globules with an average diameter around 2 μm , the salt leakage occurs over a period of time of the order of 20 days. In Figure 6, we plot the relative percentage of salt released during the first 8 days following the preparation of the double emulsion. Repeated observations under the microscope reveal a gradual decrease in the number of inner droplets with no change in size in the remaining ones. This indicates that the salt release is at least partially controlled by the coalescence of the internal droplets on the globule surface.

The scenario of release may strongly vary as a function of the double emulsion composition and colloidal size. In another series of experiments, we prepared a double emulsion with Arlacel p135 as lipophilic surfactant,

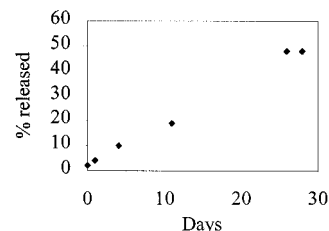


Figure 7. Rate of release of electrolyte from inner drops in double emulsions with an average globule diameter of 17 μm . System: Arlacel p135-1403/Synperonic PE/F 68/sunflower oil. The exact composition is given in Table 1.

sunflower oil, and Synperonic PE/F 68 as the hydrophilic surfactant. The detailed composition is reported in Table 1. The average globule diameter is 17 μm and the globule volume fraction is fixed at 60% (w/w). Again it can be noted that the entrapment yield after preparation is close to 98%, reflecting the high efficiency of our technique in encapsulating substances. In this particular case, the rate of release is very slow as can be observed in Figure 7. When the process is achieved (nearly 100% released), we observe under the microscope that the water droplet concentration, ϕ_i , in the globules has apparently not varied. This is confirmed by the granulometric data, since we measure a constant globule size after 2 months of storage. We therefore conclude that in this regime the salt release occurs without film rupturing, instead it occurs by an entropically driven diffusion and/or permeation of the salt across the oil globule.¹⁹

V. Conclusion

In this paper, we have found experimental conditions to obtain quasi-monodisperse double emulsions following the preliminary work that was accomplished on calibrated simple emulsions. Such materials are interesting for many applications such as hydrophilic drug encapsulation and controlled release or the preparation of "light" products, i.e., with reduced amount of fat substances. The quasi-monodispersity is an interesting property since it becomes possible to get double emulsions with reproducible and well-characterized release properties. Large quantities of these new materials may now be produced and the globule size may be tuned from 1 to 20 μm .

Besides the field of application, which may be very wide, the fragmentation of such complex materials still raises interesting fundamental questions. During the fragmentation of simple fluids, the fastest-growing wavelength of the capillary instability is typically $\lambda = r$, where r is the radius of the cylinder, so the droplet radius R is close to r . One can, therefore, wonder how the presence of droplets in the elongated thread influences the capillary instability in the regime where the final globule size approaches the internal droplet diameter. This question and others related to the fragmentation process are under current investigation.

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