

## Onset of Droplet Aggregation from Self-Diffusion Measurements in Microemulsions

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We report the first self-diffusion measurements of water-in-oil microemulsions done with fringe-pattern photobleaching-recovery techniques. These measurements give evidence of the onset of droplet aggregation which can be fairly distinct from the percolation threshold where an infinite aggregate is formed. Our results show that in some cases spherical droplets may not exist even at very low water-volume fractions. Above the observed onset, the self-diffusion coefficient reaches a nonzero limit value, reflecting the dynamical aspect of aggregation in these media.

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Microemulsions are dispersions of oil and water made with surfactant molecules.<sup>1</sup> It is currently admitted that for low water (or oil) content, the medium contains spherical water (oil) droplets surrounded by a surfactant layer and dispersed in oil (water).<sup>1-4</sup> When the microemulsions contain comparable amounts of oil and water, the droplets' structure becomes questionable. Recent x-ray scattering experiments<sup>5,6</sup> have shown that bicontinuous structures<sup>7</sup> may exist in those systems. The transition between the two types of structures are percolation transitions. They have been evidenced in water-in-oil microemulsions through electrical-conductivity measurements, around water contents of about 10%.<sup>8,9</sup> Small droplet aggregates were also qualitatively evidenced at water contents below 10%: dimers with x-ray scattering,<sup>3</sup> higher-order aggregates with electrical birefringence measurements.<sup>9</sup>

Several theories allow a description of this structural evolution.<sup>10,11</sup> They do not take into account, however, the transient character of the structures (lifetimes  $\leq 1 \mu\text{s}$ ) and they are far from being able to describe dynamical behavior in these media. The existence of transient aggregates allowing exchanges of droplet content is fundamental in the important practical application of microemulsions in chemical reactivity (catalysis, photochemistry, and solar-energy conversion, etc.). In order to gain information about these aggregates and their lifetime, we planned to perform self-diffusion measurements of a probe embedded in the interfacial layer. NMR spin-echo measurements of the self-diffusion coefficient of the surfactant molecules themselves have already been performed recently.<sup>12</sup> But surfactant molecules exchange between interfacial layers and water and oil microdomains faster than the time of the measurement: Their self-diffusion coefficient is not sensitive to droplet aggregation.

In this Letter, we report self-diffusion measurements, performed with a fringe-pattern photobleaching setup. A clear evidence of an onset of droplet aggregation is shown for the first time. Such an onset was not expected from theory.

This study was performed with a classical cationic surfactant,<sup>13</sup> the benzyldimethyl-*n*-hexadecyl-ammonium chloride (BHDC) from the British Drug Houses, which is known to form microemulsions without cosurfactant. The oil was benzene. All these products were used as received without further purification. Water was doubly distilled. The fluorescent probe was 3,3'-diethyloxadicarbocyanine iodide (DODCI) from Kodak. The droplet radius is fixed by the water to surfactant  $w_0$  ratio which is given here by weight. Four series of microemulsions were prepared with different  $w_0$ . For each series the droplet volume fraction was varied from 0 to 15%. All the experiments were performed at 20°C ( $\pm 0.1^\circ\text{C}$ ). In the fluorescence experiments, the probe concentration was always less than 5  $\mu\text{M}$  (i.e.,  $\leq 1$  probe per droplet). It should be recalled that DODCI is almost insoluble in benzene. Previous studies using picosecond spectroscopy have shown that the probe is embedded in the interfacial layer.<sup>14</sup>

The dynamic light-scattering experiments allow measurement of both the size and the polydispersity of the microemulsion droplets and characterization of the interactions between them.<sup>15</sup> These experiments have been performed with a standard setup with a (4×4)-bit Malvern correlator with delayed channels. The correlator is interfaced to a HP-9825 desk computer allowing continuous control of the base line. The scattering angle  $\theta$  was varied between 30° and 150°. The autocorrelation function of the scattered intensity was fitted with the following expression:

$$\langle I(t)I(t+\tau) \rangle = 1 + k \left\{ \exp \left[ -\frac{t}{\tau} + \frac{p}{2} \left( \frac{t}{\tau} \right)^2 \right] \right\}^2,$$

where  $\tau = 1/D_c q^2$  and  $p$  accounts for droplet-size polydispersity.<sup>16</sup>  $D_c$  is the collective diffusion coefficient and  $q$  is the scattering wave vector given by

$$q = (4\pi n/\lambda) \sin(\theta/2),$$

where  $n$  is the refractive index of the sample, and  $\lambda_0$  is the wavelength of the incident light ( $\lambda = 5145 \text{ \AA}$ ).

The variations of  $D_c$  with the volume fraction  $\phi$  of the droplets may be written (at least for small  $\phi$ )

$$D_c(\phi) = D_0(1 + \alpha\phi),$$

where  $D_0$  is the infinite dilution value of the collective diffusion coefficient and  $\alpha$  is the first virial coefficient of  $D_c$  ( $\alpha = 1.45$  for hard spheres).<sup>17</sup> The hydrodynamic radius,  $R_H$ , of the microemulsion droplet is then given by the Stokes-Einstein relation

$$D_0 = k_B T / 6\pi\eta_0 R_H,$$

where  $k_B$  is the Boltzmann constant and  $\eta_0$  is the continuous phase viscosity (here  $\eta_0 = 0.651$  cP for benzene).

Conductivity measurements were made with a Metrohm model E-518 conductometer, in order to investigate percolation phenomena.

Fluorescence recovery after fringe-pattern photobleaching (FRAP) experiments allow measurement of the self-diffusion coefficient  $D_S$  of fluorescent probes.<sup>18</sup> When strongly illuminated these probes lose their fluorescence properties (photobleaching). In the illuminated volume the fluorescence intensity is measured afterwards by use of a low-intensity light beam: The signal increases as new probes enter the studied volume and  $D_S$  can be deduced from the recovery time. These methods were improved by use of a fringe pattern and by modulation of the fluorescence signal.<sup>19,20</sup> The experimental setup we used is quite similar to the one proposed by Davoust and co-workers (see Fig. 1). The beam diameter inside the sample is about 1 mm. The bleaching pulse duration is 50 or 100 ms and the laser power at the sample is about 350 mW. The fluorescence recovery is moni-

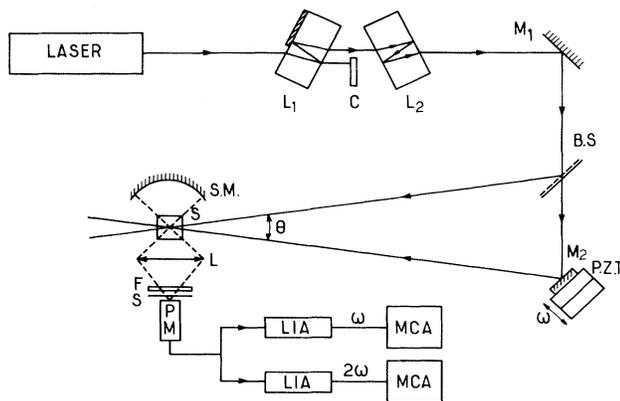


FIG. 1. Experimental setup for FRAP experiments.  $L_1$  and  $L_2$ , parallel glass plates producing perfectly superimposed beams of unequal intensity; C, chopper;  $M_1$  and  $M_2$ , mirrors; B. S., beam splitter; S, sample; S. M., spherical mirror; L, collecting lens; F, filter; S, shutter; LIA, lock-in amplifier; MCA, multichannel analyzer.

tored with a weak power beam, about  $7 \times 10^{-5}$  times lower than the bleaching power. The recovery curves were fitted by the following expression:

$$f(t) = Ae^{-t/\tau} + B,$$

where

$$\tau = i^2 / 4\pi^2 D_S,$$

$i$  is the fringe spacing, and  $D_S$  is the self-diffusion coefficient. For each sample, we checked that the recovery time scaled as  $i^2$ , and  $D_S$  was deduced from a plot of  $1/\tau$  as a function of  $q^2 = (2\pi/i)^2$ . Typical fringe spacings are in the range 10–50  $\mu\text{m}$ .

The results of the dynamic light-scattering experiments are given in Fig. 2 and Table I. For all studied samples, the polydispersity index  $p$  was always found low ( $\sim 5\%$ ). The main features of these results are that  $R_H$  increases with  $w_0$ , and  $\alpha$  decreases with  $w_0$  indicating increasingly attractive interactions between droplets.

They are similar to those obtained with other systems<sup>15</sup> and at least qualitatively well understood.<sup>21</sup> It should be noted that in our case the attractive interactions are not strong enough to lead to critical behavior and phase separation.

The formation of aggregates has been first checked through electrical-conductivity measurements (Fig. 3). Electrical percolation has been observed for all the  $w_0$

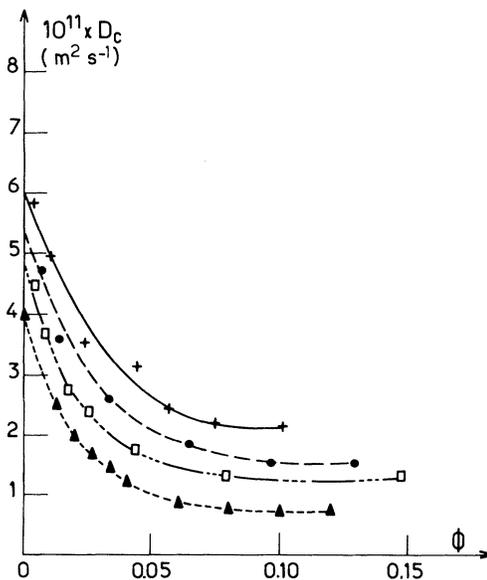


FIG. 2. Collective diffusion coefficients ( $D_c$ ) vs volume fraction ( $\phi$ ) for the four series of microemulsions at different water to surfactant ratios ( $w_0$ ): pluses,  $w_0 = 1$ ; filled circles,  $w_0 = 1.1$ ; open squares,  $w_0 = 1.25$ ; filled triangles,  $w_0 = 1.5$ .

TABLE I. Values of the hydrodynamical radii ( $R_H$ ) of microemulsion droplets and of first virial coefficients ( $\alpha$ ) for different water to surfactant ratios ( $w_0$ ).

$w_0$	$R_H$ (Å)	$\alpha$
1	55	-14
1.1	61	-19
1.25	66	-25
1.5	82	-30

values. One may observe in Fig. 3 that the percolation threshold  $\phi_p$  is displaced towards lower volume fraction when the strength of the attractive interactions increases. This effect is well accounted for by dynamic percolation models studied by numerical simulation.<sup>22</sup> These results suggest that above  $\phi_p$  an aggregate of macroscopic size is formed in the medium: The electric charges transport is then allowed through the connected water cores of the microemulsion droplets.

Typical FRAP experiments results are given in Fig. 4. The results for all the samples that have been studied are gathered in Fig. 5. For each  $w_0$  the infinite dilution value of  $D_S$  is identical to the one obtained by dynamic light scattering. This supports the idea that the probe is linked to the microemulsion droplet and that the probe does not perturb the system.

Let us consider first the case  $w_0 = 1$  or 1.1. In Fig. 5, we have a plateau up to a certain volume fraction  $\phi_c$  and then a rather sharp decrease by a factor of about 2.

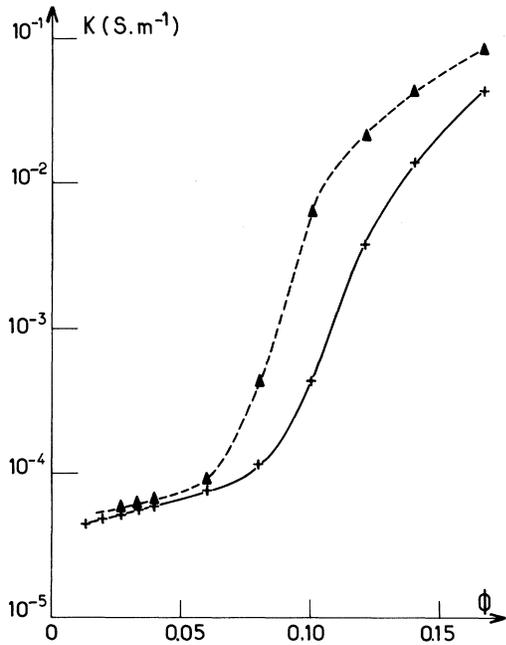


FIG. 3. Electrical conductivity ( $K$ ) vs volume fraction ( $\phi$ ):  $w_0 = 1$ ;  $w_0 = 1.5$ .

This decrease of the probe mobility can be attributed to the onset of aggregation processes in the medium. Once more the threshold value of the volume fraction is seen to decrease as the strength of the attractive interactions increases. But the decrease is more important now:  $\phi_c \sim \phi_p \sim 10\%$  for  $w_0 = 1$  and  $\phi_c \leq \phi_p/2$  for  $w_0 = 1.1$ .

For the more attractive droplets,  $w_0 = 1.25$  or 1.5, the threshold value of the droplet volume fraction is almost zero, although  $\phi_p$  is still around 8%. This indicates that droplet aggregation occurs even at very low volume fraction, and that for those systems the individual droplet picture may not be valid.<sup>23</sup>

The aggregation processes are then evidenced quite differently depending upon the type of experiments which are performed (i.e., electrical conductivity or self-diffusion). This is probably due to the different times and lengths scales involved in each type of experiment: electrical conductivity probes connectivity over extremely short times and macroscopic distances, whereas self-diffusion probes connectivity over longer times ( $\sim 1$  sec) and smaller distances ( $\sim 10 \mu\text{m}$ ).

In all cases, the nonzero value of the self-diffusion coefficient above  $\phi_c$  is indicative of the dynamical aspect of the aggregation phenomena in microemulsions: This is in contrast to what would be expected for irreversible aggregation processes.<sup>24</sup> At any time an infinite aggregate exists in the sample, but this aggregate is continuously renewed and has a finite lifetime.

In conclusion, we have observed for the first time an onset for the droplet aggregation process in water-in-oil microemulsions, which was not expected from theory. This onset is close to the percolation threshold, as evidenced by electrical conductivity measurements, for moderately attracting droplets. This means that most aggregates are formed at the same time as the infinite aggregate. The onset of aggregation occurs

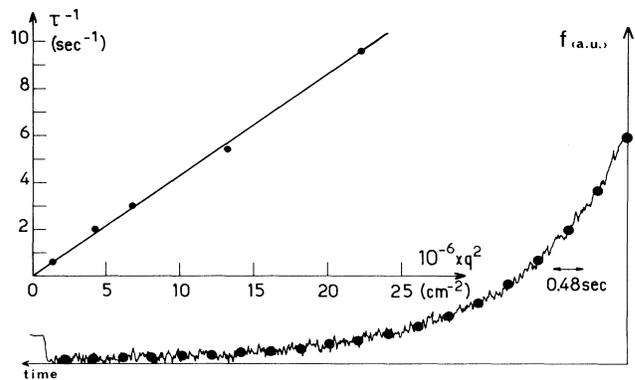


FIG. 4. Typical fluorescence recovery curve  $f(t)$  vs time. The dots are the best fit by a single exponential. In inset, linear dependence of  $\tau^{-1}$  vs  $q^2$  indicating pure diffusion phenomena.  $D_S$  is deduced from the slope.

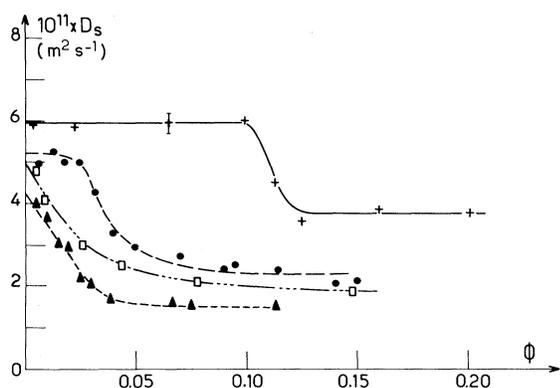


FIG. 5. Self-diffusion coefficients ( $D_S$ ) vs volume fraction ( $\phi$ ): pluses,  $w_0=1$ ; filled circles,  $w_0=1.1$ ; open squares,  $w_0=1.25$ ; filled triangles,  $w_0=1.5$ .

much earlier than percolation when attraction is larger. For large attractions, a large number of aggregates is present whatever the volume fraction is, and the description of microemulsion in terms of individual droplets is certainly not valid. We have shown that the fringe-pattern photobleaching technique is well-suited to study connectivity mechanisms in microemulsions. More work is planned with fluorescent probes either in the oil or in the water.

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<sup>23</sup>Furthermore, for all the samples studied,  $D_S$  does not vary as  $1/\eta$ , where  $\eta$  is the macroscopic viscosity. This probably reflects the nonpermanent character of the microemulsion droplets and the structural changes of the microemulsion itself upon increasing the droplet volume fraction.

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