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# Oil coating of hydrophobic surfaces from aqueous media: Formation and kinetic study

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#### Abstract

We perform oil coating of hydrophobic solid surfaces via aqueous media, from emulsions, and under the presence of a shear flow. The principle of such coating is based on the use of a system at the limit of aggregation to give rise to adhesion, with asymmetrical interfaces (oil droplet/water and solid surface/water) in order to favor the oil/surface adhesion in comparison to the oil/oil adhesion. This way, droplets stick to the solid substrate, whereas they are stable and homogeneously dispersed in the bulk. We have realized coatings from two systems of emulsions made of a mixture of hydroxy-terminated silicone oil and classical silicone oil and a mixture of sunflower oil and mineral oil. The kinetics of the coating is described by a Langmuir model where the adhesion between the oil particle and the surface is modeled as a first-order reaction. The resulting coatings are formed of oil droplets uniformly covering the solid surface. The coating density can vary with the nature of the experimental systems.

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## 1. Introduction

The formation of oil coating on solid hydrophobic surfaces is desirable in a wide range of industrial applications such as cosmetics (shampoo), fertilizers, surface protection, and pesticides.

For ecological and economic benefits, one seeks to use an aqueous solvent instead of an organic-based one. Emulsions, which are dispersions of oil droplets in water stabilized with surfactants, therefore appear as potentially suitable materials to circumvent deposition constraints. When the emulsions can be dried onto the substrate, and in the absence of dewetting effects, the droplets have time to deposit. Unfortunately, the necessary use of surfactants leads to a paradoxical difficulty for deposition application onto hydrophobic substrates, mainly for applications under rising or flow conditions. Indeed, surfactant molecules are chosen to provide repulsive interactions between the oil droplets and thereby limit their aggregation and coalescence. These surfactant molecules adsorb as well onto hydrophobic substrates and also generate repulsions between the droplets and the substrate. It thus seems difficult to combine good emulsion stability with surface deposition. It is known that emulsion droplets can be destabilized and become adhesive under well-defined conditions [1,2]. In these conditions, one can expect adhesion between droplets and solid hydrophobic substrates as well. Unfortunately, this is not yet a suitable solution to the problem since it allows the uncontrolled deposition of only a small fraction of aggregates [1,3] from a poorly stable emulsion, which rapidly creams and which is usually inhomogeneous and viscous because of the adhesion between the droplets in bulk. The homogeneous deposition of oil droplets onto an hydrophobic substrate from a stable emulsion, that

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is an emulsion comprised of repulsive droplets, is still today an open challenge. The intrinsic paradox simply comes from the hydrophobic nature of both the substrate and the oil droplets. One must induce an asymmetry in order to have strong attractive interactions between the substrate and the droplets while the droplets still experience repulsive (or weakly attractive) interactions between them. We show in this paper a general approach, based on the addition of specific additives to the oil droplets, that allows such asymmetry to be achieved.

The principle of adhesion of the emulsion oil droplet on the solid surface that we investigate in this work is based on the utilization of ionic surfactant as a sticky agent. The surfactant adsorbs onto the substrate and forms a monolayer on the substrate/water interface similar to that formed on a classical oil/water droplet interface. In the presence of salt and at low temperature, the surfactant monolayers can strongly attract each others and so the particles supporting the monolayers also become attractive and adhere to each others, e.g., oil/oil droplets and oil/solid surfaces. In the case of emulsions stabilized by ionic surfactants, e.g., sodium dodecyl sulfate, it was shown that when a sufficient amount of salt [1-3] is added the oil droplets adhere to the hydrophobic surface and between each other via the attraction of the two monolayers of surfactants adsorbed on each interface (substrate/water and oil droplet/water). However, the adhesion between the oil droplets gives rise to fractal droplet aggregates from which the substrate coating cannot be formed. To achieve asymmetric conditions, i.e., a repulsion between the droplets and an attraction between the substrate and the droplet, we add polar nonionic additives to the oil. Indeed, it has been shown that nonionic groups at the interface tend to decrease, or even to inhibit, the adhesion between ionic surfactant monolayers in the presence of salt [1,3]. The present dissymmetry of the interfaces is created by adding polar oil whose polar groups can reach the oil/water interface. We choose additives of high molecular weight which are not water-soluble. This way, they cannot reach the solid surface/water interface which remains enriched only with the sticky ionic surfactants. Of course, if the amount of additives is too high, adhesion is inhibited between both the droplets and the substrates. Conversely, if the amount of additive is too low the oil droplets become adhesive. However, by controlling the concentration of polar additives in the oil, we can find an intermediate regime in which the droplets remain repulsive but can strongly adhere to the substrate.

To gain more insight in the coating behavior of these systems, we study the adhesive behavior as a function of different factors by performing interfacial tension and contact angle measurements. The contact angle measurement are performed on large droplets, deformation of which can be accurately determined using an optical microscope. Nevertheless, these large droplets are only used to determine the adhesive energy. We used smaller droplets, which are similar to those found in practical emulsions, to investigate the kinetics of coating formation in the presence of shear flow, as a function of different parameters. We show that in our case, the coating is limited by the reaction between the colloid particles and the surface. The kinetics can be modeled by the Dabros and Van de Ven model [4] based on the Langmuir formalism. To show the general application of our findings, we use two systems of emulsion made from a mixture of classical silicone oil and hydroxy terminated silicone oil and also from a mixture of mineral oil and vegetable oil of sunflower. Finally, we conclude and we give some prospects for this work.

# 2. Materials and methods

#### 2.1. Emulsions

The oils used for this study are poly(dimethylsiloxane), abbreviated as silicone oil, and purchased from Fluka (ref. number 85414, density 0.968, viscosity at 25 °C about 100 mPa s), poly(dimethylsiloxane) hydroxy-terminated, abbreviated as Silicone OH oil and purchased from Aldrich (density 0.97, viscosity at 25 °C is about 100 mPa s), mineral oil purchased from Sigma, and sunflower oil.

The surfactant used is sodium dodecyl sulfate,  $C_{12}H_{25}$ -SO<sub>4</sub>Na, abbreviated as SDS. It is purchased from Fluka (purity >99%) and used as received.

Emulsions of oil in water are prepared using a crossflow membrane technique [5,6]. The hydrophilic porous membrane is made of polycarbonate with a pore size diameter of 1  $\mu$ m. The dispersion of about 20% oil in water is stabilized by SDS surfactant at a concentration of  $10^{-2}$  M in the aqueous phase. We obtained monodisperse emulsions characterized by a droplet size diameter *d* of 1  $\mu$ m and a polydispersity  $\Delta d/d$  of 11% as measured by a Mastersizer apparatus (Malvern) based on laser scattering measurements.

# 2.2. The substrate

We use treated surface-modified glass as a model hydrophobic collector substrate. The glass plates are cleaned according to a procedure described elsewhere [7,8]. Hydrophobization of the glass plates is done by chemical grafting of octadecyl trichlorosilane ( $CH_3-(CH_2)_{17}-SiCl_3$ ) onto the glass via a trichlorosilane group [9].

#### 2.3. The flow cell

The flow deposition experiments are carried in a parallel plate flow cell made of two hydrophobic glass plates, spaced by a Teflon spacer. The experimental dimensions of the cell are  $55 \times 13 \times 0.6$  mm<sup>3</sup>. The cell is supplied by a floodgate, an entrance, and an outgoing glass tube. The flow coming from a reservoir made of a syringe supplies the cell continuously. A syringe pump delivers the required flow rate. It can vary from 5 to 500 ml/h, yielding a Reynold number between 0.1 and 10, well within the range of laminar flow.



Fig. 1. The experimental device. The emulsion sample is injected from a syringe reservoir into the cell where the coating deposit is formed. The corresponding views are visualized by a microscope linked to a camera and a monitor and recorded by a video recorder.

#### 2.4. The experimental setup

The experimental setup, which was already described in a previous publication [10], is shown in Fig. 1. The cell is placed on the stage of a Zeiss microscope, equipped with a  $\times 50$  objective. The coating forms preferentially on the bottom side of the upper plate, where the microscopic objective is focused. The microscope is linked to a Hamamatsu camera and a monitor in order to visualize the images, which are recorded by a video recorder. They are then digitalized and treated.

#### 2.5. Data treatment

We used the NIH software for the image treatment. The image for treatment is composed of  $512 \times 512$  pixels. The pixels are characterized by a gray scale ranging from 0 to 255. The data treatment is based on the difference of contrast between pixels of stuck emulsion droplets and pixels of the droplet-free, still uncovered, substrate domains. The image is thresholded so that pixels of stuck droplets become white (their value = 255) and pixels of droplet-free substrate become black (their value = 0). The data treatment is based on the difference in contrast between the covered pixels and the uncovered ones. The image is thresholded and so results in white covered pixels (their value = 255) and black uncovered ones (their value = 0). The image is then analyzed to give a mean value consisting of a gray color value ranging from 0 to 255. The surface coating density is obtained by dividing the mean value by the white image value, 255.

#### 2.6. Energy of adhesion

The adhesive energy  $\Delta F$  is related to the resultant contact angle  $\theta$  by the Young–Dupré equation. In the case of wetting of oil droplets on solid surface,  $\Delta F_{o/s}$  is expressed by the equation

$$\Delta F_{\rm o/s} = \gamma \left[ \cos(2\theta) - 1 \right] = \gamma \left[ \cos \left( \sin^{-1} \left( \frac{r_{\rm s}}{R} \right) \right) - 1 \right], \quad (1)$$

where  $\gamma$  is the oil/water interfacial tension in the presence of surfactant,  $r_s$  is the radius of the adhesive film of the oil droplet on the solid surface, and *R* is the radius of the oil droplet (Fig. 2a).

In the case of adhesion between an oil droplet and a macroscopic flat oil surface, the adhesive energy  $\Delta F_{o/o}$  is expressed by

$$\Delta F_{\text{o/o}} = 2\gamma \left[ \cos(\theta) - 1 \right] = 2\gamma \left[ \cos\left(\frac{1}{2}\sin^{-1}\left(\frac{r_{\text{o}}}{R}\right)\right) - 1 \right],$$
(2)

where  $r_0$  is the radius of the adhesive film of the oil droplet on the oil surface and R is the radius of the oil droplet (Fig. 2b).

We perform adhesive energy measurements by analyzing the shape of the deformed oil droplets.

Emulsions of large oil droplets ( $\approx$ 50 µm) are prepared by shaking a system composed of 5% oil in an aqueous SDS solution (10<sup>-2</sup> M) and at a given NaCl salt concentration (varied from 0.4 to 0.8 M). Cells made of hydrophobic glass are filled by these emulsions and then placed on the microscope stage. Note that large droplets are used because they can be more easily accurately characterized.



Fig. 2. Optical micrograph of silicone OH oil droplet adhesion on (a) hydrophobic glass surface and (b) oil surface. The area delimited by the bright circle in the center of the oil droplet corresponds to the adhesive flat film between the oil droplet and the surface. Experimental parameters are: oil concentration = 5%, SDS concentration =  $10^{-2}$  M, NaCl concentration = 0.6 M (the black bar corresponds to 37.5 µm). (c) Schematic representation of the adhesion of the oil particle on the surface through the surfactant monolayers which allows the oil droplet to form a contact angle  $\theta$ .

The contact angle is determined from optical transmission microscopy observations, as was done previously for other systems of oil droplets in water [1] and water droplets in oil [11]. It consists in measuring the radii of flat adhesive films between oil droplet interfaces and solid interfaces (Fig. 2a) and also the radii of the adhesive films of adhesive oil interfaces (oil droplets on oil surfaces (Fig. 2b)). The contact angle value is determined by averaging 10 measures.

On the other hand, the surface tension  $\gamma$  was determined using the pendant drop technique [12]. We study the case of formation of water droplets in oil media.

The adhesive energy is then calculated according to Eq. (1) or (2). The net energy between two droplets of smaller size, which is of interest in practical applications, can now be deduced by simply multiplying the surface energy by the contact area of the droplets.

# 3. Results and discussion

In this work, our objective is to form a coating of micrometer-sized oil droplets on hydrophobic surfaces and under shear flow. We study the effect of several parameters on the coating formation.

# 3.1. Effect of polar oil concentration/asymmetrical interfaces

We recall that the adhesion between the oil particle and the surface results from the attraction in the presence of salt (condition close to the precipitation of the surfactant) [2,3] between the two monolayers of ionic surfactant adsorbed on both interfaces (oil/water and surface/water). This allows the oil particle to stick to the surface and to form a contact angle  $\theta$  (Fig. 2c). Note that the adhesive film is essentially composed of a surfactant bilayer confining a few hydration water molecules. Its thickness is about 29 Å [13].

Fig. 3 shows the evolution of the adhesive energy as a function of NaCl concentration for different silicone oil compositions (silicone oil/silicone OH oil) in SDS aqueous solutions ( $10^{-2}$  M) at room temperature ( $T \cong 25$  °C).

For NaCl concentrations smaller than 0.4 M, the adhesive energies oil droplet/oil droplet  $\Delta F_{o/o}$  and oil droplet/surface  $\Delta F_{o/s}$  are equal to zero for all oil compositions. Adhesive



Fig. 3. Energy of adhesion between the oil droplets and between the oil droplets and the solid surface as a function of salt concentration for different oil compositions: silicone oil, silicone OH oil and 5% silicone OH oil/95% silicone oil.

films could be observed neither between oil particles nor between oil particles and the surface. For salt concentrations of about 0.4 M, contact angles which reveal the adhesive character of the droplets can be observed ( $\theta \neq 0$ ). They have undergone a transition from a nonadhesive to an adhesive state. This transition happens either between oil droplets or between oil droplets and surface. It occurs at a given salt concentration, which strongly depends on temperature [2]. As NaCl salt concentration increases further, the adhesive energies droplet/droplet  $\Delta F_{o/o}$  and droplet/solid surface  $\Delta F_{o/s}$  increase for all oil compositions. Note that the same evolution takes place, e.g., the adhesive energies increase, as the temperature decreases [2] for a given salt concentration. Equivalent evolution of adhesive energy between hexadecane oil droplets as a function of salt concentration has already been reported [2]. The same behavior is observed between identical interfaces (oil/oil interfaces) and between different interfaces (oil/water and hydrophobic surface/water).

When the silicone OH concentration increases the droplet/droplet  $\Delta F_{o/o}$  and droplet/surface  $\Delta F_{o/s}$  adhesive energies decrease. More importantly, for 100% silicone OH oil,  $\Delta F_{o/s}$  is higher than  $\Delta F_{o/o}$ . However, for 100% silicone oil the situation is inverted and the adhesive energy  $\Delta F_{0/0}$  is higher than the adhesive energy  $\Delta F_{o/s}$ . For the composition 5% silicone OH oil/95% silicone oil, the emulsion is more adhesive than that of 100% silicone OH oil and less adhesive than that of 100% silicone oil. At that composition,  $\Delta F_{o/s}$  is still slightly higher than  $\Delta F_{o/o}$ . As polar oil groups (hydroxy OH groups) are added to the nonpolar oil, the adhesive energy decreases. Indeed, these nonionic groups play the role of co-surfactants, they can reach the oil/water interface and contribute to the bilayer structure with the SDS surfactant. Similar behavior between hexadecane oil droplets was observed for emulsions stabilized with SDS mixed with nonionic surfactant NP10 in the presence of NaCl salt [2]. The adhesive energy between oil droplets decreases drasti-



Fig. 4. Schematic representation of the asymmetrical interfaces adhesion concept. (a) When the droplets and the substrates are in adhesive conditions and covered by the same surfactant molecules, adhesion is observed in bulk between the droplets and on the substrate as well. (b) Addition of polar, but non-water-soluble oil (represented by big black amphiphilic macromolecules) to the emulsion droplets and introduced into the oil phase of the emulsion before its preparation allows a dissymmetry to be created between the droplet/droplet interaction and the droplet/substrate interaction. Under such conditions, deposition of oil droplets onto the substrates become possible even with droplets that remain stable and homogeneously dispersed in the bulk, as required in a large number of applications.

cally with the NP10 concentration. Note that the same behavior is observed, e.g., the adhesive energy increases as salt concentration increases and temperature decreases, for one-component interfaces made only from SDS molecules and two-component interfaces made from SDS and nonionic molecules. In our case, we cannot use nonionic surfactants, even lipophilic ones, to create the dissymmetry because they can reach the solid surface via the SDS micelles. Under such conditions, the droplet/solid surface adhesion energy will also be decreased and the sticking of the oil particles on the surface will be prevented. The nonionic group must be linked covalently to the oil to not reach individually the solid surface/water interface. High-molecular-weight polar oil remains trapped in the oil droplets.

It emerges from these experimental results that the adhesion between mixed component layers is very sensitive to the concentration of the nonionic groups. This behavior explains why the presence of a small amount of hydroxy groups at the oil/water interface, only about 5% of silicone OH oil, can be sufficient to favor the oil droplet/substrate interaction in comparison to the oil droplet/oil droplet interaction. For instance, for the oil/solid surface interaction the adhesion is based on the attraction between two distinct monolayers: a mixed system made of SDS and OH-terminated molecules at the oil/water interface and a pure monolayer made only of SDS molecules at the solid/water interface. However, the droplet/droplet interaction involves two similar mixed monolayers of SDS and OH-terminated molecules (Fig. 4).

The fact that for 100% silicone oil  $\Delta F_{o/o} > \Delta F_{o/s}$  means that the SDS layer structure at the oil/water interface is not identical to the SDS layer structure at the surface/water interface.

So the addition of polar oil is necessary to determine the conditions where the droplet/droplet interaction is weaker

than the droplet/solid surface interaction. The oil droplets can stick on the surface and not to each other. Indeed, a homogeneous coating can form only from individual oil droplets and not from fractal oil aggregates [14] grown in the bulk emulsion.

When the system is at the limit of aggregation and asymmetrical interfaces are achieved, a uniform and controlled oil coating can be grown.

Fig. 5a shows the evolution of the surface coating density as a function of time, from two emulsions made of 100% silicone OH oil and 5% silicone OH oil/95% silicone oil (the experimental parameters are oil concentration = 0.1% in volume, NaCl concentration = 0.38 M, SDS concentration =  $10^{-2}$  M, and the flow rate = 50 ml/h).

Fig. 5b shows the evolution of the surface coating density as a function of time, from two emulsions made of 100% sunflower oil and 5% sunflower oil/95% mineral oil (the experimental parameters are oil concentration = 0.1% in volume, NaCl concentration = 0.4 M, SDS concentration =  $10^{-2}$  M, and flow rate = 50 ml/h). Fig. 5c shows some views of the resulting coating at different times.

We note first that for all systems, the surface coating density increases with time. The same curve shape is obtained for all the studied systems with a coating rate decreasing with time.

For the silicone oil system, the composition 5% silicone OH oil/95% silicone oil gives a higher coating surface density with faster coating kinetics. This result implies that the emulsion made from 5% silicone OH oil/95% silicone oil is more adhesive than that made from 100% silicone OH oil, which is in agreement with the previous findings about adhesive energy.

The same kind of evolution is obtained for mineral/sunflower oils. Moreover, the maximum surface coating density is higher for the emulsion made of 5% sunflower oil/ 95% mineral oil than that from 100% sunflower oil.

It is interesting to remark that the maximum surface coating density is higher for the emulsion made of 5% sunflower oil/95% mineral oil than for that made of 5% silicone OH oil/95% silicone oil.

# 3.2. Effect of shear rate

Fig. 6 shows the evolution of the surface coating density as a function of time, from an emulsion made from 5% sunflower oil/95% mineral oil, for different shear rates from 50 to 200 ml/h (oil concentration = 0.1% in volume, NaCl concentration = 0.4 M, SDS concentration =  $10^{-2}$  M).

We should note first that for all the studied systems at different shear rates, there is no desorption of the adhesive oil particles from the surface with time. Once a droplet is stuck, the shear at the interface is too weak to remove the droplet.

It emerges from these experimental results that the shear rate has no effect on the coating kinetics. This means that the kinetics is not limited by the diffusion of the oil particles on the surface but only by the reaction between the oil particle and the surface.

In this regime, according to the Dabros and Van de Ven model [5] based on the Langmuir formalism, the surface coating density is expressed as a function of an adsorption rate constant  $k_{ad}$  and a desorption rate constant  $k_{des}$ , it scales with time *t* as follows:

$$S(t) = \frac{S(\infty)}{1 + k_{\rm des}/k_{\rm ad}c_{\rm p}} \left[ 1 - \exp(-(k_{\rm ad}c_{\rm p} + k_{\rm des})t) \right].$$
(3)

 $S(\infty)$  is the surface fraction covered at infinite time. It can be much lower than 1 because of geometrical constraints, shadow effects (due to hydrodynamic interactions between the deposited particles and the flowing ones [15]), and repulsive interactions between particles and also because of microheterogeneity of the surface.

Since there is no desorption of particles during the coating process, the experimental results can be compared to the Van de Ven model in the particular case where  $k_{des} = 0$  (Langmuir model). The surface coating density is expressed simply as follows:

$$S(t) = S(\infty) \left[ 1 - \exp(-(k_{ad}c_p)t) \right].$$
(4)

We fit our experimental data with Eq. (4) (Langmuir model) using two adjustable parameters,  $k_{ad}$  and  $S(\infty)$ . Fig. 7 shows the validity of this simple approach to model the obtained results. The fit yields a value of 0.008 s<sup>-1</sup> for the adsorption rate  $k_{ad}$  and 0.63 for  $S(\infty)$ .

Finally, we remark that the colloidal coatings are isotropic and no structuration appears even at high shear rate (500 ml/h).

#### 3.3. Effect of salt concentration

Fig. 8 shows the evolution of the surface coating density as a function of time *t* for two salt concentrations.

It appears that when the salt concentration decreases, the coating kinetics decreases. The emulsion is less adhesive according to the adhesive energy measurements. The experimental data are fitted according to Eq. (4). The constant rate  $k_{ad}$  is very sensitive to the NaCl concentration:  $k_{ad} = 0.01 \text{ s}^{-1}$  and  $S(\infty) = 0.29$  for NaCl concentration = 0.38 M,  $k_{ad} = 0.0054 \text{ s}^{-1}$  and  $S(\infty) = 0.25$  for NaCl concentration = 0.35 M. As a consequence, the probability that an oil particle stick on the surface decreases.

It is also of great interest to stress that the constant rate  $k_{ad}$  seems to be directly related to the adhesive interaction between the oil droplet and the surface. This means that a kinetic study can provide useful information about the interactions between the droplets and a given substrate. For systems where contact angles cannot be easily or routinely measured, such as industrial emulsions made of small droplets, the flow cell experiment, in addition to directly model application conditions, can enlighten our fundamental understanding of the nature of the interactions between substrates and emulsion droplets.



Fig. 5. Evolution of the surface coating density as a function of time *t* for two emulsions made of 100% silicone oil and 5% silicone OH oil/95% silicone oil (a) and of 100% sunflower oil and 5% sunflower oil/95% mineral oil (b). Experimental conditions are oil concentration = 0.1%, NaCl concentration = 0.38 M, SDS concentration =  $10^{-2}$  M, and flow rate = 50 ml/h. (c) Optical micrograph as time elapses of the coating for an emulsion of 5% sunflower oil/95% mineral oil. Experimental conditions are oil concentration =  $10^{-2}$  M, and flow rate = 50 ml/h. (c) Optical micrograph as time elapses of the coating for an emulsion of 5% sunflower oil/95% mineral oil. Experimental conditions are oil concentration = 0.1%, NaCl concentration = 0.4 M, SDS concentration =  $10^{-2}$  M, and flow rate = 50 ml/h (the black bar corresponds to 37.5 µm).



Fig. 6. Effect of the shear rate on the kinetics of coating from an emulsion of 5% sunflower oil/95% mineral oil. Experimental conditions are oil concentration = 0.1%, NaCl concentration = 0.4 M, SDS concentration =  $10^{-2}$  M, and flow rate = 50 ml/h.



Fig. 7. The fit of the experimental data according to Eq. (5) (the Langmuir model) for the emulsion made of 5% sunflower oil/95% mineral oil. Experimental conditions are oil concentration = 0.1%, NaCl concentration = 0.4 M, SDS concentration =  $10^{-2} \text{ M}$ , and flow rate = 50 ml/h.



Fig. 8. Evolution of the coating density as a function of time for different salt concentrations. Experimental conditions are oil concentration = 0.1%, SDS concentration =  $10^{-2}$  M, and flow rate = 50 ml/h. The full lines correspond to the fit of the experimental data according to Eq. (4).



Fig. 9. Evolution of the coating density as a function of time for different oil concentrations for an emulsion made of 5% silicone OH oil/95% silicone oil (a) and 5% sunflower oil/95% mineral oil (b). Experimental conditions are NaCl concentration = 0.38 M, SDS concentration =  $10^{-2}$  M, and flow rate = 50 ml/h. The full line corresponds to the fit of the experimental data according to Eq. (4).

#### 3.4. Effect of oil particle concentration

Figs. 9a and 9b show the evolution of the coating kinetic as a function of time t, for emulsions of different oil concentrations made by 5% silicone OH oil/95% silicone oil and 5% sunflower oil/95% mineral oil, respectively.

It appears that the kinetics of the coating increases as the oil concentration increases. For both systems and for all oil concentrations, the experimental data fit are again well fitted with Eq. (4), where the coating rate is proportional to the oil particle concentration. The constant rate  $k_{ad}$  remains constant as the oil particle concentration varies.

We deduce from this experimental result that way to increase the coating kinetics, keeping all the other parameters constant, consists in increasing the oil concentration of the emulsions. Flow cell experiments can be valuable to quantitatively evaluate the effect of oil concentration for practical situations.

### 4. Conclusion

We have formed a monolayer oil droplet coating on hydrophobic solid surfaces from aqueous media (from emulsion) and in the presence of a shear flow.

To realize these coatings, two conditions must be satisfied. First, the system (emulsion) should be at the limit of aggregation to give rise to adhesion by, in this case, adding salt. Second, the oil droplets should adhere on the surface and not between each others. This dissymmetry is created by addition of polar oil to the initial formulation.

In this study, we have used two systems of emulsions differing by the nature of the oil mixture: silicone oil/silicone OH oil and mineral oil/sunflower oil. The resulting coatings are isotropic and the kinetics of their formation are limited by the sticking reaction between the oil particle and the surface. The Langmuir model, where the adsorption is a first-order reaction, is in very good agreement with the experimental data for all the investigated systems.

We hope that these results will help the development of new emulsion formulations to be deposited onto solid substrates such as cosmetics, pesticides, and paints. In addition, we stress that the experimental approach used in this work may serve, not only to determine optimal conditions for emulsion coatings, but also to investigate subtle features of surface interactions between emulsion droplets and solid substrates. Indeed, even though we do not perform direct force measurements, we have experimentally shown that the formation kinetics and the density of emulsion coatings are very sensitive to surface interactions. Therefore, simple flow cell deposition experiments may be particularly helpful to advance our fundamental knowledge of emulsion/substrate interactions.

As an extension of this work, it will be interesting to investigate the effect of rinsing on the colloidal coating such as the residual surface coating density; this case concerns applications such as shampoo. Finally, it will be also interesting to investigate the oil coating on hydrophilic surfaces via other types of attractive interactions between the particles and the surface like the coating of negatively charged surface by emulsions stabilized by anionic surfactant via cationic polyelectrolyte layer.

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#### References

- [1] M. Aronson, H.M. Princen, Nature 286 (1980) 370.
- [2] P. Poulin, J. Bibette, Langmuir 15 (1999) 4731.
- [3] P. Poulin, Thesis, Université de Bordeaux I, 1995.
- [4] T. Dabros, T.G.M. Van de Ven, J. Colloid Interface Sci. 89 (1982) 232.
- [5] R. Katoch, Y. Asano, A. Furuya, K. Sotoyama, M. Tomita, J. Membr. Sci. 113 (1996) 131.
- [6] L. Zhang, J. Hu, Z. Lu, J. Colloid Interface Sci. 190 (1997) 76.
- [7] J.B. Brzoska, N. Shahidzadeh, F. Rondelez, Nature 360 (1992) 719.
- [8] J.V. Davidovits, Thesis, Université de Paris 6, 1998.
- [9] J.B. Brzoska, I. Ben Azouz, F. Rondelez, Langmuir 10 (1994) 4367.
- [10] W. Essafi, P. Poulin, S. Chiron, B. Bavouzet, Langmuir 20 (2004) 123.
- [11] P. Poulin, J. Bibette, Langmuir 14 (1998) 6341.
- [12] W.D. Harkins, F.E. Brown, J. Am. Chem. Soc. 41 (1919) 499.
- [13] P. Poulin, F. Nallet, B. Cabane, J. Bibette, Phys. Rev. Lett. 77 (1996) 3248.
- [14] P. Poulin, J. Bibette, Phys. Rev. Lett. 79 (1997) 3290.
- [15] I. Pagonabarraga, J. Bafaluy, J.M. Rubi, Phys. Rev. Lett. 75 (1995) 461.