

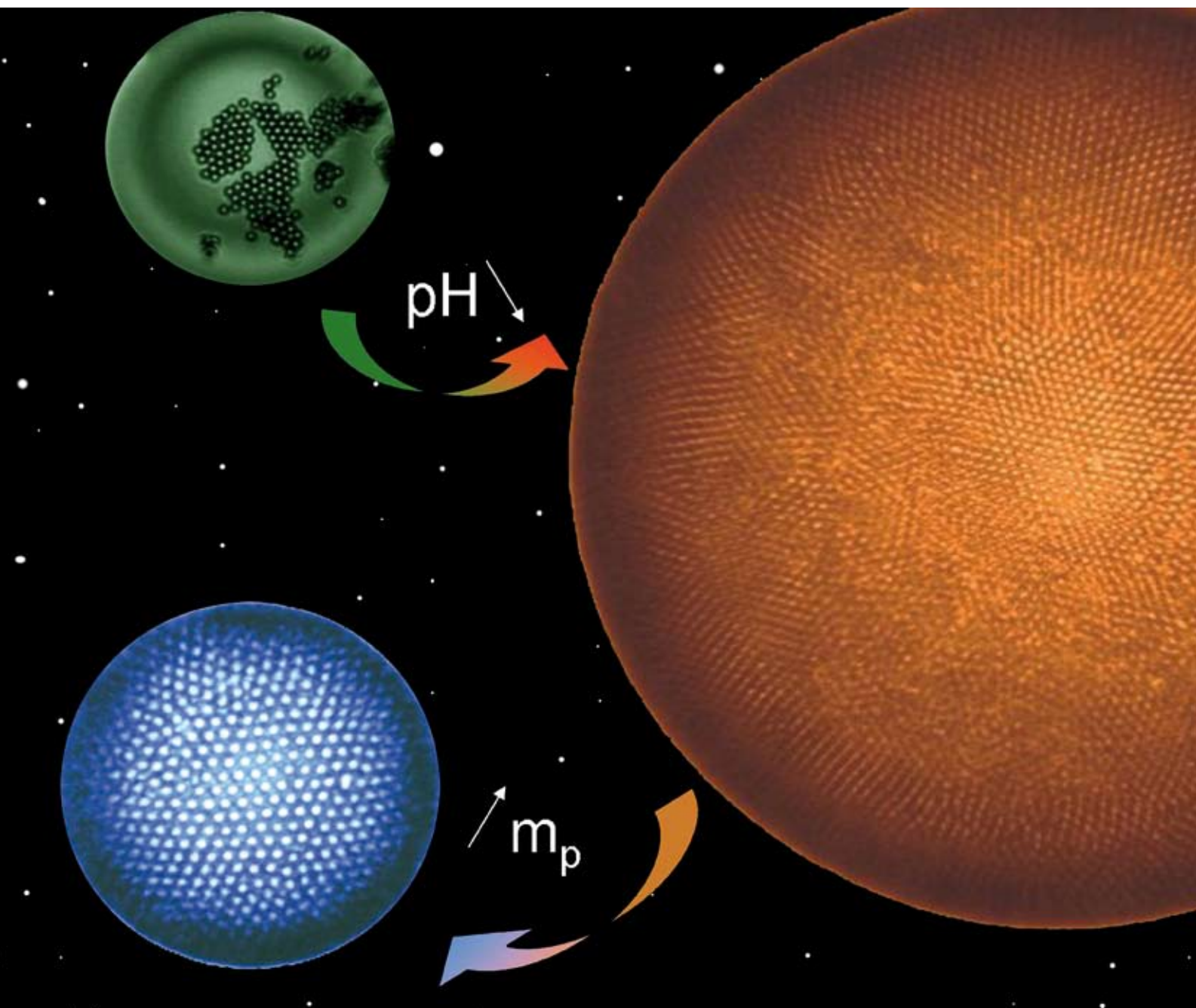
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THEMED ISSUE

Colloidal particles at liquid
interfaces



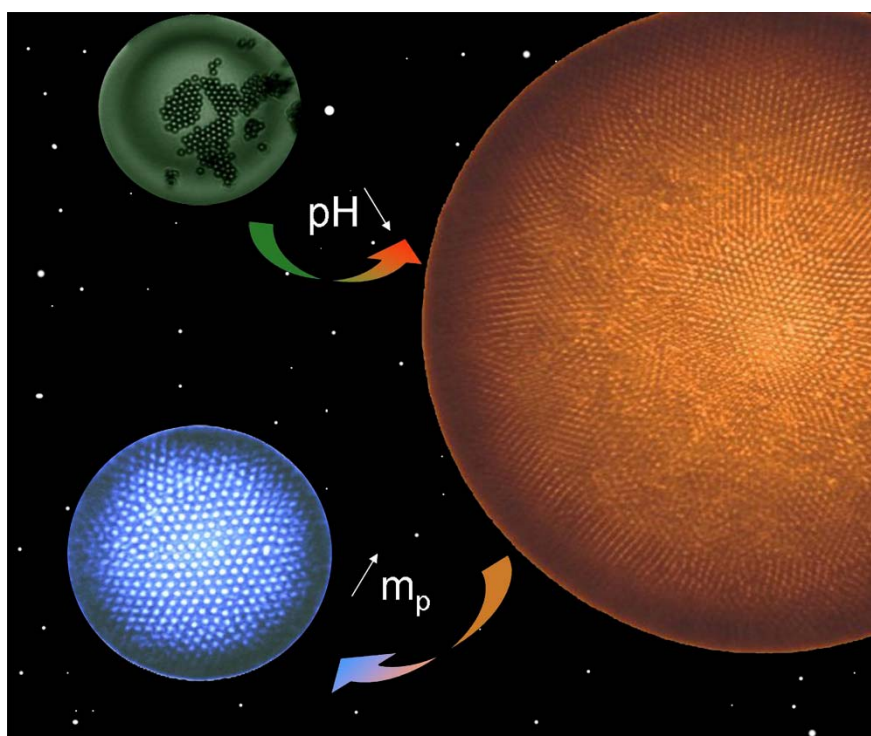
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Colloidal particles at liquid interfaces

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Pickering emulsions with stimulable particles: from highly- to weakly-covered interfaces†

Florent Gautier,^a Mathieu Destribats,^a Romain Perrier-Cornet,^b Jean-François Dechézelles,^a Joanna Giermanska,^a Valérie Héroguez,^b Serge Ravaine,^a Fernando Leal-Calderon^{*c} and Véronique Schmitt^a

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We study oil-in-water emulsions stabilised by pH-sensitive colloidal silica or latex particles. Depending on the composition of the continuous phase, the same type of particles and the same emulsification process lead to emulsions characterised either by large drops densely covered by the particles, or to small droplets which are weakly covered. The two kinetically stable states can be tuned reversibly by using pH or salinity as compositional stimuli. We examine the emulsions' behaviour in these two limiting cases and we discuss the possible mechanisms allowing stabilisation, especially in the case of low surface coverage.

1. Introduction

Pickering^{1,2} or solid-stabilised emulsions are surfactant-free metastable dispersions of two non-miscible fluids kinetically stabilised by colloidal particles.^{3–5} Such emulsions exhibit remarkable kinetic stability and allow a reduction in the use of hazardous surfactants. Recently, we produced Pickering emulsions using strongly flocculated particles in water.^{6–9} Highly monodisperse emulsions were obtained with low particle numbers exploiting the so-called limited-coalescence process.^{8,10} Once the agitation was stopped, coalescence occurred and was suddenly halted when the interface was densely covered either by a monolayer of particles or by particle aggregates, depending on the energy input during emulsification. Therefore, by adjusting both the stirring intensity and the particle number, Pickering emulsions could be formulated in a large droplet-size range (from $\approx 1 \mu\text{m}$ to $\approx 1 \text{ mm}$). The mechanical behaviour of the interface was also examined. The experimental data provided evidence for the existence of rigid interfacial layers that originated from the very strong attractive interactions between colloidal particles within the interface.⁹ This surface rigidity certainly determined the remarkable resistance of concentrated droplets against coalescence. The lateral interactions between particles adsorbed at the oil/water interface are therefore a very important issue within the prospect of controlling the inter-

facial properties and consequently the stability of Pickering emulsions.

From a practical point of view, the design of emulsions which can evolve under the effect of an external stimulus is a real challenge, and the possibility of destabilizing them “on demand”, by simply modifying a compositional variable in the system, is a topic of current investigation.¹¹ An abundance of literature^{12–17} is especially devoted to pH-sensitive particulate emulsifiers, where a moderate pH variation may induce a transition between the initially-dispersed state and partial or total macroscopic separation of the oil and water phases because of particle desorption. The aim of this paper is somewhat different: we use pH- and salt-responsive particles that remain adsorbed as a means of tuning the average droplet size and controlling the relative kinetic stability of the emulsions. Two limiting situations have been identified: using the same amounts of particles, water and oil, we show that it is possible to stabilise either large drops densely covered by the particles (low pH or high salt content) or, more surprisingly, small droplets weakly covered (high pH). We compare the relative emulsion stability in these two limiting situations and we discuss the possible stabilisation mechanism in the poorly-covered regime.

2. Experimental

2.1 Materials

The dispersed oil was hexadecane ($\rho = 0.77 \text{ g cm}^{-3}$) of high purity (>99%), purchased from Aldrich and used without further purification. The continuous aqueous phase was prepared with water of Milli-Q quality (resistivity = $18.2 \text{ M}\Omega \text{ cm}$). For silica synthesis, tetraethoxysilane also termed tetraethyl orthosilicate (Fluka), aminopropyltriethoxysilane (Aldrich), absolute ethanol (Prolabo) and ammonia solution (29% in water, JT Baker) were used. The materials used for latex synthesis are described elsewhere.¹⁸

^a Université Bordeaux 1, Centre de Recherche Paul Pascal, CNRS UPR 8641, Avenue du Dr Albert Schweitzer, 33600 Pessac, France

^b Laboratoire de Chimie des Polymères Organiques, Université Bordeaux 1, CNRS, ENSCPB UMR 5629, 16 Avenue Pey-Berland, 33607 Pessac, France

^c Laboratoire des Milieux Dispersés Alimentaires, Université Bordeaux 1, Avenue des Facultés, 33405 Talence, France. E-mail: f.leal@istab.u-bordeaux1.fr; Fax: +33 (0)5 56 37 03 36; Tel: +33 (0)5 40 00 83 86

† The HTML version of this article has been enhanced with colour images.

2.2 Particle synthesis

Two types of hydrophilic particles were synthesised (mineral and organic) and their surface was partially hydrophobised in order to make them suitable for adsorption at the oil/water interface.

2.2.1 Silica particles. Silica particles were synthesised according to procedures already reported in the literature.^{19,20} A primary population of silica particles was synthesised according to the well-known Stöber sol–gel process²¹ (hydrolysis and condensation) and then functionalised by grafting aminopropyltriethoxysilane molecules in order to render the surface pH-sensitive. The added quantity of grafting agent was adjusted to obtain 15 functions per nm² of the nanoparticle surface. The obtained particles were characterised by a statistical analysis from TEM images (Fig. 1a). Their mean diameter was estimated to be (145 ± 5) nm and their density was 2.1 g cm^{-3} . The particles were purified by centrifugation–redispersion cycles, with each successive supernatant being replaced with pure water. The extent of purification was assessed by measuring the surface tension of the serum until the value was close to that of water. The particle concentration was determined by measuring the mass of a dried extract.

2.2.2 Latex particles. Micron-sized monodisperse polymer particles with a core–shell structure were prepared through a two-step polymerisation process. First, highly cross-linked core particles were prepared through precipitation polymerisation of a mixture of monomers (divinylbenzene and ethyleneglycol dimethacrylate) in hot acetonitrile, following a procedure described elsewhere.²² Incorporation of a co-monomer such as chloromethylstyrene in the mixture of monomers endowed the polymer core particles with reactive chlorine functions at their surface,²³ allowing atom-transfer radical polymerisation of *tert*-butylacrylate in a second step. Finally deprotection of the *tert*-butyl groups through acidolysis in dichloromethane, in the presence of trifluoroacetic acid, led to polymer particles with a hairy and hydrophilic shell structure that enabled easy dispersion of the particles in water. For more details concerning the fabrication process and the elimination of all the reaction residues, the reader can refer to the paper of Reculosa *et al.*¹⁸ The particles were remarkably uniform in size (Fig. 1b) and they were characterised by a mean diameter of $3.5 \mu\text{m}$, determined by static light-scattering (Malvern Mastersizer). Because of their large size, the particles were not subject to Brownian motion and they tended to sediment rapidly in the water phase.

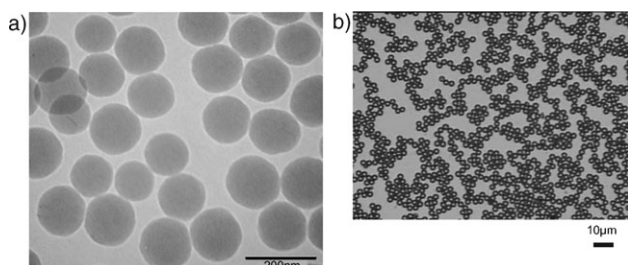


Fig. 1 (a) TEM image of the silica particles. (b) Microscopic image of the latex particles.

2.3 Particle dispersion

The particles were dispersed in water at the appropriate pH and were then sonicated (350 W for 30 min with a Bioblock Scientific 88155 sonicator). The pH was adjusted by addition of small amounts of either HCl or NaOH in order to sweep a large range of pH: from 1 to 14 for latex particles and from 3 to 8 for silica particles. In the case of silica particles, the range was restricted in order to avoid particle dissolution. The salinity was then fixed independently by addition of appropriate amounts of NaCl. We chose to avoid the use of commercial pH-buffer solutions in order to control the salinity. Conductivity measurements showed that pH adjustments by NaOH or HCl did not significantly modify the ionic strength.

2.4 Emulsion preparation

Hexadecane-in-water emulsions were prepared in batches of 20 g according to the following protocol. A mixture of 20 wt% of hexadecane and 80 wt% of the aqueous phase containing the particles was vigorously shaken by hand. Although simple, this method produced emulsions in a reproducible fashion, *i.e.* with the same final average diameter and size distribution. It was also possible to shake emulsions which had been prepared earlier and find that the final droplet-size distribution did not vary, suggesting that the final state in terms of droplet-size distribution was mainly determined by the system composition.

Here arises the question of knowing whether the kinetic stability of the emulsions is due to the particles or to the presence of chemical residues from the synthesis steps. We checked that the same samples prepared without particles were not stable for more than one hour whatever the pH or ionic strength. Moreover the successive supernatants of the centrifugation steps were used as aqueous phase to prepare new emulsions. No stable emulsions could be obtained in such conditions. These two experiments reveal that only particles were able to impart kinetic stability whatever the emulsion's composition.

2.5 Definition of the interface coverage C

We checked that particle anchoring at the oil/water interface was always complete and irreversible. Indeed, we did not observe the presence of free particles in the continuous phase after the emulsification step. As a consequence, monodisperse solid-stabilised emulsions were produced exploiting the limited coalescence process.⁸ It consists of producing a large excess of oil/water interface compared to the amount that can be covered by the solid particles. For this process to occur, a very small number of solid particles is required as is the case in our experiments. When the agitation is stopped, the partially unprotected droplets coalesce, thus reducing the total area of oil/water interface. Since the particles are irreversibly adsorbed, the coalescence process stops as soon as the oil/water interface is sufficiently covered. The resulting emulsions exhibit a drop diameter that is controlled by the mass of particles. Assuming that all the particles are adsorbed at the

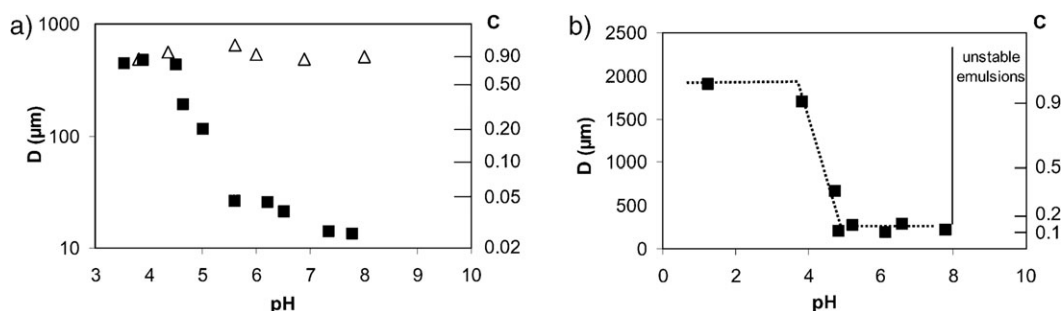


Fig. 2 (a) Influence of pH on the emulsion drop size for emulsions stabilised by the 144 nm silica particles (■) without added salt, (Δ) with 0.1 M NaCl. (b) Influence of pH on the emulsion drop size for emulsions stabilised by the 3.5 μm latex particles. Rapid destabilisation was observed for $\text{pH} > 8$.

oil/water interface, the final drop diameter D is given by:⁸

$$\frac{1}{D} = \frac{m_p}{4C\rho_p d_p V_d} \quad (1)$$

where m_p is the mass of particles, ρ_p is the particle density, d_p is the particle diameter, V_d is the volume of the dispersed phase and C is the surface coverage *i.e.* the fraction of the droplet interfacial area covered by the particles. This parameter characterises the packing density of the particles at the interface. For example, for hexagonally-close-packed monodisperse particles C is equal to 0.9.

2.6 Zeta-potential measurements

The ζ -potential was estimated from the measurement of the particle electrophoretic mobility with a Malvern Zetasizer 3000 HSA instrument employing a dip cell, and the Smoluchowski equation was used for converting the measured mobilities. In order to avoid multiple-scattering effects, the dispersions were highly diluted in a water phase at the appropriate pH prior to the measurements.

2.7 Droplet-size measurements

For emulsions with diameter lower than 100 μm , the size distribution was obtained using a Malvern Mastersizer granulometer and Mie theory. The size distribution was characterised in terms of the surface-averaged diameter D and polydispersity P :

$$D = \frac{\sum_i N_i D_i^3}{\sum_i N_i D_i^2} \quad \text{and} \quad P = \frac{1}{D} \frac{\sum_i N_i D_i^3 |\bar{D} - D_i|}{\sum_i N_i D_i^3} \quad (2)$$

where N_i is the total number of droplets with diameter D_i and \bar{D} is the median diameter, *i.e.* the diameter for which the cumulative undersized volume fraction is equal to 50%.

For emulsions with drop sizes larger than 100 μm and sufficiently dispersed to be observed, the size distribution was estimated by image analysis obtained with an inverted optical microscope (Zeiss Axiovert X100). Images were recorded and the dimensions of about 50 droplets were measured so that both the surface-averaged diameter D and the polydispersity P , defined by eqn (2), could be estimated.

3. Results—emulsion behaviour

3.1 Influence of pH

The influence of pH on the final drop mean diameter at fixed composition is reported in Fig. 2a for emulsions stabilised by the silica particles (16 g of aqueous solution containing 11 mg of silica particles and 4 g of hexadecane) and in Fig. 2b for the latex-stabilised emulsions (9 g of aqueous solution containing 10 mg of latex particles and 1 g of hexadecane). In the absence of NaCl, as pH was increased from 3 to 8, the size exhibited more than a tenfold decrease. The effect of pH disappeared when salt was added (0.1 M NaCl) and no variation of the droplet size was visible (Δ in Fig. 2a). The emulsion droplets rapidly creamed and we checked that the lower continuous phase did not contain any particles. Hence, assuming that particles arrange themselves as a monolayer at the oil/water interface, the mean surface coverage C can be calculated as a function of pH, using eqn (1). To facilitate the reading, a scale for C has been added as a right-hand axis in Fig. 2.

For both types of particles at low pH, the emulsions were characterised by a C value close to 0.9. The emulsions were remarkably monodisperse with a polydispersity index P always smaller than 20% (Fig. 3a). These observations were similar to those reported by Arditty *et al.*^{6,8} for silicon oil-in-water emulsions stabilised with *n*-octyltriethoxysilane functionalised silica particles. Such high values of C are compatible with a closely-packed monolayer of the particles at the interface, in agreement with the observations under the microscope reported in Fig. 4a.

As pH was increased (Fig. 2a and b), the mean surface-coverage parameter C decreased drastically, reaching surprisingly low values. Taking advantage of their large size, the latex particles at the interface could be easily visualised by optical

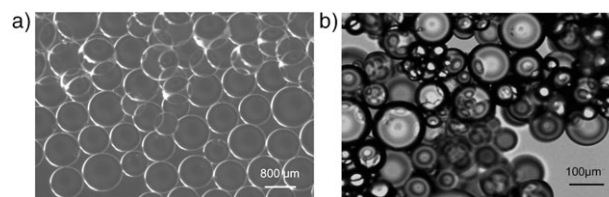


Fig. 3 Macroscopic aspect of the emulsion composed of 4 g hexadecane and 16 g aqueous solution containing 7.25 mg silica particles (a) at $\text{pH} = 4$ and (b) at $\text{pH} = 8$.

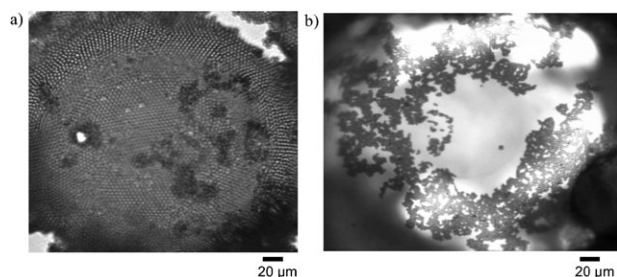


Fig. 4 Microscope image of an emulsion drop covered by latex particles (a) pH = 1 and (b) pH = 4.8.

microscopy (Fig. 4b). One distinguishes that the coverage is non-uniform due to 2D particle clustering and that large drop areas are not covered at all. Despite this low level of surface coverage, emulsions were quiescently stable over months (at least 6 months) even in the creamed state where the volume fraction was of the order of 60% at the top of the samples. Hence drops in close contact did not coalesce and appeared highly flocculated (Fig. 3b). Kinetically stable emulsions with low surface coverage have already been evidenced by Vignati *et al.*²⁴ using fluorescent silica particles. They report that “no straightforward relation exists between the degree of droplet surface coverage and macroscopic emulsion stability”. Tarimala and Dai²⁵ also observed that polystyrene particles form small patches with local hexagonal order separated by other particle-free domains.

3.2 Influence of salt concentration

In order to determine the influence of salt, water was replaced by various aqueous brines. The resulting emulsion droplet size as a function of NaCl concentration is reported in Fig. 5 for the silica particle-stabilised emulsions (16 g of brine containing 7.25 mg of silica particles and 4 g hexadecane, pH = 6). For salt concentrations lower than 0.04 M and larger than 0.07 M, the emulsions were monodisperse with a drop size of the order of 70 µm and 800 µm respectively. For intermediary salt concentrations (0.04 to 0.07 M), two drop populations with well-defined sizes (70 and 800 µm) were initially observed with variable relative proportions: at low NaCl concentration (0.04 M), small drops were much more abundant than at higher concentration (0.07 M) (Fig. 6). After a few days of quiescent storage, the small drops disappeared and the distribution became monomodal. Indeed, no variation in the drop size was observed at low (<0.04 M) or high salt contents (>0.07 M).

Again, the mean surface coverage C was calculated, revealing that drops were poorly covered ($C = 0.08$) in the low-salt

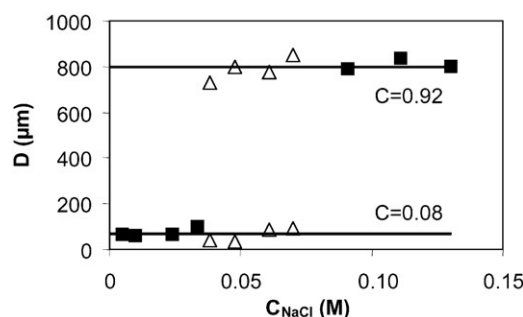


Fig. 5 Influence of NaCl concentration at pH = 6 for silica-stabilised emulsions: (■) unique drop population, (△) initially bimodal distribution.

regime whereas, the surface coverage was dense ($C = 0.92$) at high salt concentration.

3.3 pH or salt cycling/bi-stability

In order to determine whether the size evolutions due to pH or salt were reversible, we modified the aqueous-phase composition for silica particle-stabilised emulsions cyclically. Beginning with an emulsion at pH = 6, the lower phase after emulsion creaming was replaced by an aqueous solution at pH = 4.5. Then, the emulsion was carefully homogenised several times by gentle manual inclination of the vessel to avoid droplet fragmentation. The drop size increased in a few seconds when lowering the pH. When raising the pH from 4.5 to 6, the system had to be re-emulsified as the size decrease requires energy supply and the obtained droplet size was the same as for the emulsion initially prepared at pH = 6 (Fig. 7a).

The same kind of procedure was applied with a 0.1 M NaCl brine at pH = 6, beginning with an aqueous solution without salt (Fig. 7b). The replacement of the lower phase with appropriate salinity was repeated 10 times to ensure a precise control of the salt concentration. As for pH cycling, the transition from small to larger drops happened without external energy supply whereas the transition from large to smaller drops required intense manual shaking.

For both parameters (pH and salinity), the resulting sizes were perfectly reproducible at each cycle showing that the emulsion can adopt two kinetically stable states, characterised by two different degrees of surface coverage.

3.4 Influence of the mass of particles

The influence of the mass of particles was explored for different pH and salinity conditions. In Fig. 8a and 8b, we report the evolution of $1/D$ as a function of m_p , for silica-

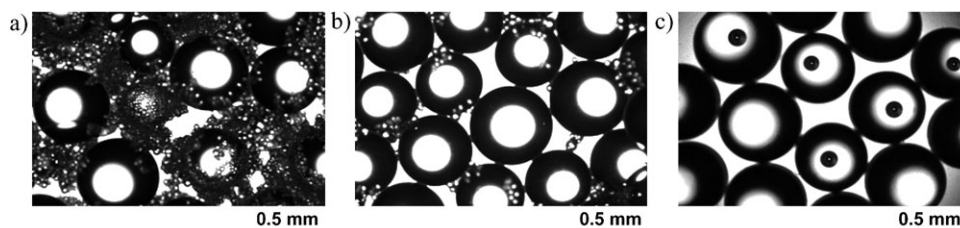


Fig. 6 Microscopic images of the resulting emulsion at (a) 0.04, (b) 0.06 and 0.12 M NaCl.

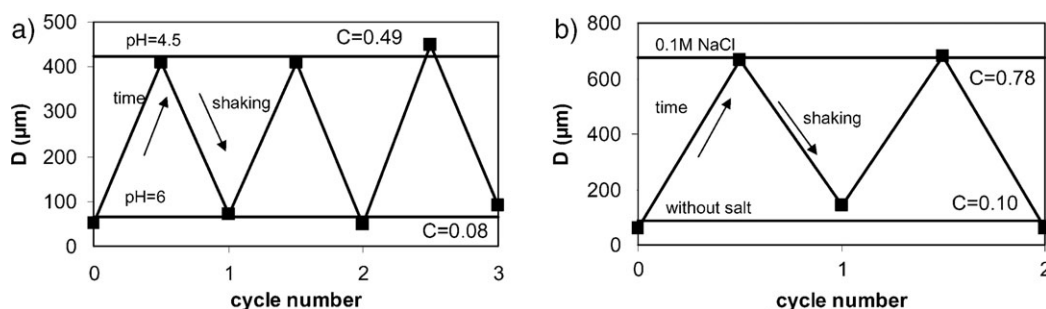


Fig. 7 (a) Influence of pH cycling on the emulsion drop size for an emulsion stabilised by silica particles. When pH was decreased, the emulsion was quiescently stored and the size evolved spontaneously. When pH was increased, the emulsion was re-emulsified. (b) Influence of salinity cycling on the emulsion drop size at pH = 6. When salinity was increased, the emulsion was quiescently stored and the size evolved spontaneously. When salinity was decreased, the emulsion was re-emulsified.

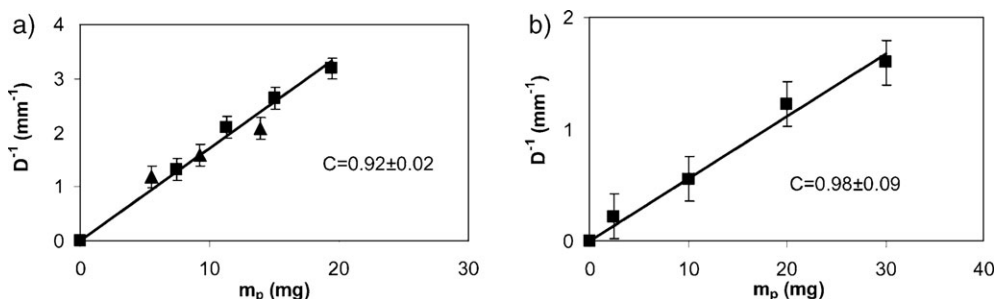


Fig. 8 Influence of the mass of particles on the drop size for emulsions stabilised by (a) silica particles at pH = 4 and (b) latex particles at pH = 1. The inverse of the drop diameter has been plotted in order to evidence its linear dependence with m_p as expected from eqn (1).

stabilised emulsions at pH = 4 and for latex-stabilised emulsions at pH = 1. The inverse drop size varies linearly with the mass of particles, all the other parameters being constant, in agreement with eqn (1). The surface coverage C is deduced from the slope and the value obtained is in agreement with a closely-packed arrangement of the particles ($C \approx 0.92$). For silica-stabilised emulsions, the same experiments were performed at pH = 6 (Fig. 9) with and without NaCl. The linear dependence of $1/D$ vs. m_p again suggests that a limited coalescence process is at the origin of the final droplet size. However, it is clear from the value of the surface coverage measured in the absence of salt, $C \approx 0.08$, that cessation of coalescence is not provoked by a dense packing of the particles. Whatever the pH, when salt was added we obtained

a C value close to 0.8 reflecting a dense covering by the particles.

At pH = 8, the emulsions were highly flocculated (in the absence of salt) and it was not possible to accurately estimate the drop size.

4. Characterisation of suspension behaviour and emulsion stability

In this section, we shall try to correlate the behaviour of the particles dispersed in the water phase with their packing at the oil/water interface. We shall also characterise the relative stability of poorly- and densely-covered droplets.

4.1 Suspension behaviour

We prepared aqueous dispersions of silica particles at fixed particle mass fraction of 3.5% and at different pH values. In Fig. 10a, we report a photograph showing the state of the dispersion 30 min after preparation. The particles are well dispersed whatever the pH except in the intermediary range, from 5.5 to 6.5, where rapid sedimentation occurs, revealing bulk particle aggregation. We also measured the ζ -potential of the silica particles as a function of pH (Fig. 11). The ζ -potential reflects the charge density, which in our case, is fixed by both the NH_2 groups of the aminopropyltriethoxysilane-grafted molecules and the SiOH groups of the bare silica surface. The isoelectrical point of the particles is reached for a pH of the order of 6, consistent with the aggregated state of the aqueous suspension (Fig. 10a) due to the absence of electrostatic repulsion. For pH values below or above the

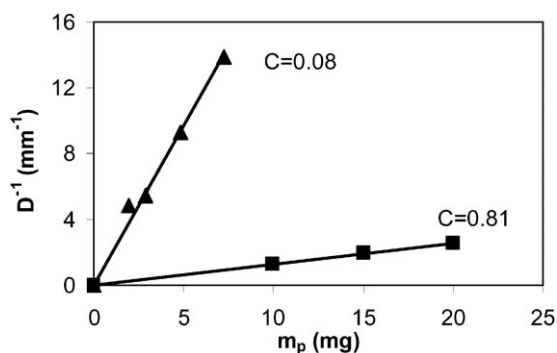


Fig. 9 Influence of the mass of particles at pH = 6 with (■) and without salt (▲) on the emulsion drop size for emulsions stabilised by silica particles.

isoelectrical point, the particles are significantly charged so that the electrostatic repulsion protects them against aggregation as revealed by Fig. 10a. When 0.1 M NaCl is added, the particles aggregate and sediment in less than 15 minutes whatever the pH (Fig. 10b), most probably because of the salt-induced electrostatic screening effect. Unfortunately, we could not reliably measure the ζ -potential of the latex particles because of their large size and rapid sedimentation (non-Brownian character).

Considering the whole set of observations, we come to the conclusion that the behaviour of the particles in the bulk phase and the interfacial coverage are not straightforwardly correlated. Indeed, for the silica-stabilised emulsions, we have found situations where the droplet surface is either densely- (pH = 4) or poorly-covered (pH = 8) and in both cases, the particles are perfectly dispersed in the bulk aqueous phase. It is worth emphasising that bulk and interfacial interactions may significantly differ. The bulk behaviour is dominated by electrostatic, steric and van der Waals interactions, while for particles located at the interface, in addition to the previous forces the net lateral interaction is also influenced by dipolar²⁶ and capillary forces.²⁷

4.2 Emulsion stability

Considering the low surface coverage at high pH, the emulsions exhibit a really astonishing stability at rest even for volume fractions as high as 60%. In order to test the mechanical resistance of the interfaces towards compression, we submitted two emulsions characterised by two distinct surface coverages to centrifugation for more than 4 h in order to reach a stationary state, at different centrifugation rates. Centrifugation causes concentration at the top of the samples and promotes drop coalescence above some compression threshold. Two compressed droplets will begin to deform before their interfaces actually touch, due to the intrinsic repulsive interactions between them. Emulsions minimize their total free energy by reducing the repulsion at the expense of creating some additional surface area by deforming the droplet interfaces.^{28,29} The necessary work to deform the droplets arises from the application of an external osmotic pressure Π defined as the derivative of the free energy F with respect to the total volume V at constant dispersed volume V_0 . By measuring both

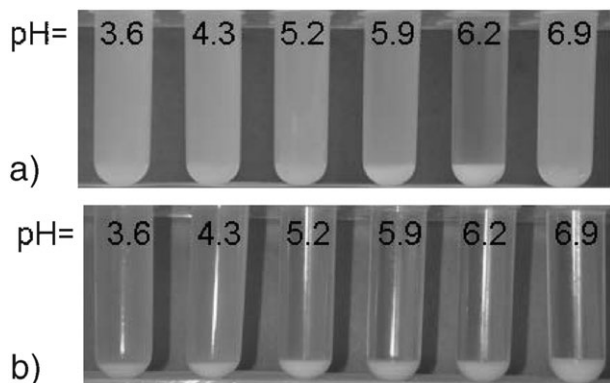


Fig. 10 Phase behaviour of silica suspensions (at 3.5 wt%) as a function of pH (a) without added salt, (b) with 0.1 M NaCl.

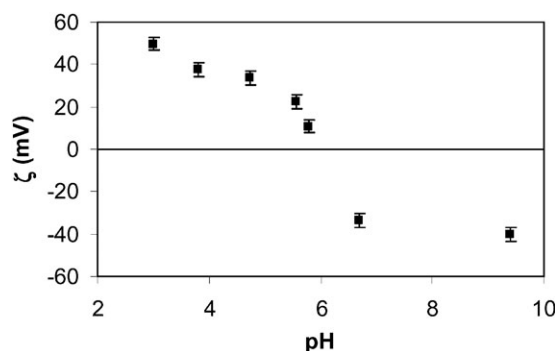


Fig. 11 Evolution of the ζ -potential for silica particles as a function of pH.

the height h of the creamed phase and the emulsion final volume fraction ϕ_f , the osmotic pressure Π can be calculated following eqn (3):²⁸

$$\Pi = -\left(\frac{\partial F}{\partial V}\right)_{V_0} = |\Delta\rho|\phi_f\omega^2\left(dh - \frac{h^2}{2}\right) \quad (3)$$

where $\Delta\rho$ is the density mismatch between the dispersed and continuous phases, ω is the centrifugation speed and d the distance between the emulsion and the rotor (Fig. 12). We define Π^* as the osmotic threshold pressure above which a layer of oil appears at the top of the tube. Since the osmotic pressure is expected to vary as the inverse drop size,^{10,29} Π^* has been normalised by $1/D$ to allow comparison. In Table 1, we report the values obtained with an emulsion stabilised by 7.25 mg of silica particles at pH = 6. For densely-covered interfaces (presence of NaCl), this stress is 4 to 5 times larger than for poorly-covered interfaces (no NaCl). In Table 1, Π^*D reflects the maximal 2D stress the interfaces can bear. For densely-covered interfaces (with salt), this stress is 4 to 5 times larger than for poorly-covered interfaces (absence of salt).

The stability can also be compared by measuring the maximum oil fraction that can be incorporated during the emulsification process, keeping the oil-to-particle ratio constant. For poorly-covered interfaces, this limit is estimated to be of the order of 65 vol% whereas it is of the order of 80% vol for densely-covered interfaces.

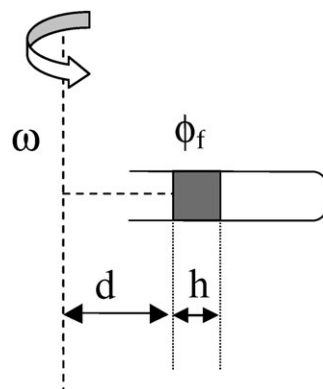


Fig. 12 Scheme of the centrifugation experiment.

Table 1 Osmotic resistance limit for two differently covered silica-stabilised emulsions at pH = 6

	$D/\mu\text{m}$	C	Π^*/Pa	$\Pi^*D/\text{mN m}^{-1}$
Emulsion without salt	55	0.08	1.26	0.07
Emulsion with 0.1 M NaCl	786	0.8	0.42	0.33

From these experiments, we conclude that even if all the emulsions are quiescently stable, the ones with high surface coverage are significantly more resistant to compression.

5. Discussion

Emulsification was performed in conditions such that the energy supply allowed creation of an excess of oil/water interface and irreversible anchoring of the particles. In all cases, coalescence occurs until a certain degree of surface coverage is achieved. Two limiting situations have been identified. In some cases, coalescence stops when the particles form a dense monolayer at the interface protecting the drops against further recombination. In other situations, coalescence stops well before a closely-packed arrangement of the particles at the interface is achieved and the emulsions are strongly flocculated. In this limit, large domains remain unprotected and the issue that naturally arises is that of understanding why coalescence is arrested at such an early stage. In the following, we propose two different mechanisms to account for this observation: one is based on the formation of particle bridges (Fig. 13a) and the other on the attractive interaction that naturally arises between particles adsorbed on two neighbouring interfaces (Fig. 13b and c).

Recently, direct-observation experiments were performed^{30–35} in which particle-covered interfaces were brought into contact in a controlled manner. When the two interfaces were close enough, the particles at both interfaces spontaneously arranged in such a way that the particles at one interface filled the interstices of particle lattices on the opposing interface, followed by a rapid growth of a dense particle aggregate of disc shape that resisted further coalescence between the two interfaces. The particle aggregate was found to be only one monolayer thick that spanned the two interfaces, which is consistent with the bridging configuration. In our case, a similar mechanism could be operative which would explain both the aggregated state of the droplets and the low

degree of surface coverage. As coalescence proceeds, the droplet surface-to-volume ratio becomes progressively smaller, until the number of particles per droplet becomes high enough to allow formation of large interfacial disc-shaped aggregates that inhibit further coalescence.

Vignati *et al.*²⁴ presented evidence of a possible role of the particle dynamics on the stabilisation of poorly-covered droplets as they recorded the motion of fluorescent particles. They also reported on “reallocation effects” associated with droplet closeness. In quite a few situations where surface coverage was low, they captured images of droplet pairs where fluorescence intensity was higher near the contact region, bespeaking enhanced local colloidal concentration either in the continuous phase or within the droplet interfaces. In order to explain the possible accumulation of particles at droplet contact, we propose a second mechanism based on dipole–dipole interactions between the particles adsorbed onto two neighbouring interfaces. In this approach, we neglect droplet curvature and the contact zone is considered as being formed by two parallel flat interfaces (Fig. 13). This assumption is reasonable considering the huge difference in radius between particles and droplets. A charged particle anchored at one interface between polar and non-polar media produces an effective dipole because of the surface-charge difference in the two different media.²⁶ The interaction energy w between anti-parallel dipoles anchored on two interfaces depends on the angle, α , between the dipole direction and the centre-to-centre line (Fig. 13b) as:

$$w \propto 3 \cos^2(\alpha) - 1$$

The dipole–dipole interaction is attractive for α larger than 54.7° with a growing intensity as α increases. Therefore the system tends to adopt a configuration where α takes the largest accessible value. This situation occurs when the particles anchored at one interface are in contact with the opposing interface (Fig. 13c). The upper limit, α_{max} , is fixed by the particle wettability, which is itself determined by the contact angle θ . For particles preferentially wetted by water as it is the case here, θ is expected to be smaller than 90° .³ From simple geometrical considerations, α_{max} and θ are related through:

$$\cos(\alpha_{\text{max}}) = \frac{1 - \cos(\theta)}{2}$$

For $0 \leq \theta \leq 90^\circ$, α_{max} is always larger than 54.7° , and thus the dipolar interaction is always attractive. This simple dipolar description allows an accumulation of particles at the drop contact to be accounted for, which could explain the emulsion stability in the case of very low surface coverage. It is also consistent with the observed flocculated state of the emulsions. However it does not explain the pH dependence. Indeed, the observed phenomena are not symmetric with respect to the particle surface charge. In the case of functionalised silica particles, the ζ -potential measurements show that at low or high pH the particles are oppositely charged with comparable absolute values of the surface potential (Fig. 11) while the drop surface coverage is very different for these two pH limits. This surprising result requires further investigations.

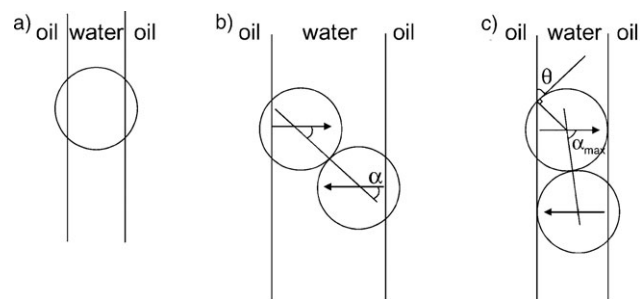


Fig. 13 Proposed stabilising mechanism for poorly-covered interfaces: (a) particle bridging, (b) particles adsorbed onto neighbouring interfaces behave as anti-parallel dipoles, (c) the system adopts an optimal configuration.

6. Conclusion

The experiments performed with different types of particles (mineral or organic) and different surface charges reveal the occurrence of kinetic bi-stability: the emulsion can be stabilised either by a very dense particle layer at the interface or by particle patches, probably located at the drop contact. In this latter situation very small amounts of particles are required to impact stability ($62 \text{ m}^2 \text{ g}^{-1}$ for silica particles and $8.5 \text{ m}^2 \text{ g}^{-1}$ for latex particles). We have proposed two distinct microscopic mechanisms to explain the origin of the kinetic stability in this low surface-coverage limit. A deeper understanding requires a specific study concerning the interactions between particles located on the same interface and on two distinct interfaces.

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