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Particles with tunable wettability for solid-stabilized emulsions

Yukari Sakazaki, Véronique Schmitt, and Ulf Olsson

Abstract
We demonstrate that the wettability of cosmetic grade, silica-coated titanium dioxide nanoparticles may be tuned by simply soaking them in a cyclic silicone oil. This allows for tuning the type of emulsion that they stabilize, from oil-in-water to water-in-oil. By analyzing the sedimentation of water-in-oil emulsions, the effect of the soaking time (wettability) on drop size and drop-drop interactions was investigated. From centrifugation experiments performed up to emulsion breakage, we obtain an effective water-oil interfacial tension for the particle-loaded interfaces, which indicate lateral particle-particle interactions. Finally, we demonstrate that the proposed particle functionalization is terminated upon addition of water followed by emulsification. In addition, it is irreversible and can be accelerated through heating.

1. Introduction
In solid-stabilized emulsions, commonly known as Pickering emulsions, solid particles are used as stabilizers instead of surface-active compounds such as surfactants or amphiphilic polymers. In this kind of emulsion, particles are irreversibly anchored at the oil-water interface forming a mechanical barrier against coalescence of liquid droplets. There is increasing interest in Pickering emulsions among the industrial fields such as cosmetics, pharmaceutics and food industry, since solid-stabilized emulsion system enables avoiding the use of surfactants, or at least, reducing their concentration in a large extend. Such a will is guided by the fact that, using surfactant, sometimes raises concerns about negative effects on human skin or on the environment.

In solid-stabilized emulsions, the type of emulsion formed, oil-in-water (O/W) or water-in-oil (W/O) depends on different factors. Finkle et al. reported that the type of emulsion depends on the wettability of particles. It has also been reported that the preparation process could influence the emulsion type. In addition, emulsion composition, that is to say component ratio, such as water to oil ratio, particle concentration and hydrophilic to hydrophobic particles ratio has also been reported as determining factors. Physical and chemical properties of the components such as particles size and shape, oil polarity and oil viscosity, pH value and presence of electrolyte in the aqueous phase also affect emulsion type and stability. Among all these parameters, the particle wettability, corresponding to the relative hydrophobicity/hydrophilicity, seems however to be the most important one.
Silica particles are known to be hydrophilic due to the presence of silanol groups at the particle surface. In order to confer them the ability to adsorb at an oil/water interface, they need to be partly hydrophobized. The most widespread way of functionalizing silica particles or wafers is to graft, using a coupling agent, some hydrophobic moieties at their surface as for example silane groups, amine or vinyl groups or even complex structures. Moreover, in the field of reinforcement, hydrophilicity of silica particles was undesirable as it was known to induce particle agglomeration in organic solvent as the ones often present in paints or varnishes. Numerous efforts have therefore been dedicated to silica surface modification in order to increase the particle hydrophobicity for various applications. Indeed, silica particles are often used as fillers into polymeric matrices and their surface hydrophobization modifies significantly their dispersion state and consequently the rheological properties of the material. Functionalized silica particles were also used to produce superhydrophobic and/or oleophobic cotton textiles. Adhesion enhancement between a PDMS elastomer and a flat silica surface, end-grafted with PDMS chains, has been evidenced when adsorption of PDMS chains occurred additionally to grafting. Association of silica particles and PDMS has also been proven to highly enhance antifoaming efficiency as compared to each component alone. In their paper, Marinova et al. proposed a progressive hydrophobization of silica particles at room temperature and showed the existence of a maximum efficiency in antifoaming that depended on the used surfactant. During the silica-PDMS compound preparation, process parameters, such as heating and stirring, accelerated hydrophobization. A more complete and systematic study of the phenomenon, with model ca. 500 μm-sized glass beads, led the authors to conclude about the mechanism, the amount of hydrophobized surface, the role played by the surfactant and the effect of the treatment protocol on how to tune the particle hydrophobicity and hence the contact angle and the stability of the particle loaded interfacial film.

2. Experimental section

2.1. Materials

Two different silica coated titania particles, that we refer to as P1 and P2, respectively, were investigated as emulsions stabilizers. Both particles have a diameter of ca. 34 nm and were obtained from Showa Denko K.K., Japan. The P1 particles are composed of 80 wt. % TiO₂ and 20 wt.% SiO₂, and are inherently hydrophilic. The P2 particles are the same as P1, except that they in addition have been hydrophobically modified by grafting PDMS (poly(dimethylsiloxane), dimethicone) chains with a molecular weight of circa 1000 g/mole. The grafted chains make up 7% of the total particle weight.

Before using the particles they were left to dry for 30 minutes at 80 °C. In all experiments, Decamethyl cyclopentasiloxane (M₉₉ ≈ 370 g/mole, SH245, Dow Corning Toray Co., Ltd.) was used as the oily phase. Purified water, passed through a Millipore purifier (Milli-Q Reagent Water system) was used as the water phase.

Samples were prepared by weighing the components. Weight fractions were transformed into volume fractions using ρ_0 = 1.0 g/cm³ for the water density, ρ_0 = 0.96 g/cm³ for the oil density and ρ_p = 3.8 g/cm³ as the density of the P1 and P2 particles. This value has been calculated using a TiO₂ density of 4.23 g/cm³ and a SiO₂ density of 2.65 g/cm³.

2.2. Preparation of emulsion samples

Powder of dry particles and silicone oil were put into glass vessel and this mixture was kept at 25 °C for a certain period of time, that we call the soaking time, t_s. The weight fraction of particles in the oil, W_p = m_p/(m_p + m_o), where m_p
and $m_o$ are the masses of particles and oil respectively, was always kept constant to $W_p = 0.0125$. This corresponds to a fixed volume fraction of particles with respect to oil $\phi_p = 0.0032$. After soaking for time $t_s$, the powder was dispersed using an ultrasonic processor (Vibracell VCX130 with 3 mm tip diameter, Sonics & Materials) operating at 20 kHz for 5 minutes. Then the appropriate amount of water was added, and the mixture was emulsified by continuing sonication for an additional 5 minutes. For the samples used to assess the type of emulsion formed, 0.01 wt% of Eosin bluish was added to the water phase.

In some particular experiments the emulsion samples were stored at 25°C for a certain period of time, called the maturing time, $t_m$ in order to investigate whether there was a time evolution of the emulsion properties. After storage, a part of each sample was re-sonicated for 5 minutes while the other part of the same sample was centrifuged at 40,000 RCF until the emulsions were completely broken and separated into three layers: an upper oil phase, a middle water phase and a particle sediment. After removing both silicone oil and water, particles were washed three times with ethanol (cyclopentasiloxane is soluble in ethanol) and dried under reduced pressure at room temperature. New emulsion samples were then prepared using this powder following the same procedure as previously described without additional soaking time.

### 2.3. Emulsion characterization

#### 2.3.1. Assessment of emulsion type

The type of emulsion oil-in-water (O/W) or water-in-oil (W/O) was assessed by macroscopic and microscope observations. Emulsions containing or not the hydrophilic dye (Eosin bluish) were observed in an optical microscope (Zeiss Axioplan Universal microscope) and by observation of emulsion creaming (O/W) or sedimentation (W/O).

#### 2.3.2. Observation and drop size determination

Observation with the optical microscope also allows for an estimate of the drop size and gives a visual indication about the polydispersity of the emulsion and the presence or absence of excess particles in the continuous phase.

#### 2.3.3. Measurement of sedimentation

To investigate the sedimentation of W/O emulsion droplets, samples were put into 5 mm NMR tubes and left to stand. The interface between the white sediment and the excess oil phase at the top of the tube was sufficiently sharp to determine a time evolving sediment height, $h(t)$, to be compared to the constant total sample height, $h_0$. The initial sedimentation rate, $v_{in}$, was determined from the initial slope, $v_{in} = -d(h/h_0)/dt$ at $t = 0$.

#### 2.3.4 Stability in an ultracentrifugal field

The stability of the particle loaded interfacial film was investigated by centrifugation of the the emulsions and observing emulsion breakage. W/O emulsion samples in 5 mm NMR tubes were centrifuged (3K30, SIGMA Laborzentrifugen GmbH) at 25°C. The RCF was gradually increased in 100 g steps ($g = 9.81 m/s^2$) each 10 minutes until free water was observed signaling emulsion breakage.

### 3. Results and discussion

The unmodified (P1) and hydrophobically modified (P2) silica coated TiO$_2$ particles were left to “soak” in the oil during a time $t_s$ (soaking time). After this time, the particles were dispersed by 5 minutes of sonication after which the appropriate amount of water was added and the samples were emulsifiedsonication for an additional 5 minutes (see Experimental section for details). The resulting emulsions were characterized with respect to emulsion type, sedimentation rate and resistance to breaking by centrifugation. The results are presented and discussed below.

#### 3.1. Emulsion type

Emulsions with different water volume fractions in the range $0.1 \leq \phi_w \leq 0.8$ were prepared after different soaking times. The resulting emulsion types are presented in $t_s$-$\phi_w$ stability diagrams, shown in Figure 1a and 1b, for P1 and P2 particles, respectively. As can be seen, the soaking time has a significant effect on the emulsion type formed in the case of P1 while soaking had no visible effect on the already modified particles, P2.

In the case of the P1 particles (Figure 1a) and up to 6 h of soaking, emulsions are of the O/W type irrespective of the water-to-oil ratio (WOR). The notation O + O/W + (W) means that the entire amount oil is not emulsified. A layer of un-emulsified oil lays on the top of the O/W emulsion and this direct emulsion has creamed over an aqueous phase. For longer soaking times ($t_s > 6h$), reverse W/O emulsions were formed as long as oil is the main component i.e. at lower water content ($\phi_w < 0.4$). At higher water content, double emulsions, O/W/O or W/O/W, were observed. Thus, as an effect of increased $t_s$, we observe for lower water contents a transition from an O/W to a W/O emulsion, indicating that the soaking leads to a transformation of the P1 particles from hydrophilic to hydrophobic. In the case of P2 particles (Figure 1b), on the other hand, the emulsion type is not affected by the soaking time. It is worth noticing that the type of emulsions depends strongly on the water-to-oil ratio, $\phi_w/\phi_o$. Indeed up to $\phi_w \approx 0.35$, which means that oil is the predominant phase, emulsions are W/O while at larger water contents ($\phi_w \geq 0.45$), the emulsions are O/W. In a limited zone ($0.35 < \phi_w < 0.45$), the two types of emulsions coexist in the form of double emulsions. This seems reminiscent from the formulation/composition maps proposed by Salager and co-workers for surfactant-stabilized emulsions. In these latter cases, for $\phi_w/\phi_o \approx 1$, the type of emulsion is governed by the formulation, i.e. the affinity of the surfactant towards the aqueous or oily phase. At high water or oil content $\phi_w/\phi_o$ tends to govern the type of emulsion. As a consequence, when formulation and composition agree, the type of emulsion is
unambiguous, while if there is a conflict between formulation and composition double emulsion are often observed. In these regions of the map, the emulsion type becomes very sensitive to the preparation protocol pathway. For the titanium dioxide particles studied in the present paper, the presence of double emulsion could also reveal the uncertainty of the system to choose between two opposite tendencies arising from the particle wettability on the one side and from the emulsion composition on the other side.

Particle wettability, or hydrophilicity/hydrophobicity balance, is usually quantified in terms of the contact angle, $\theta$, at the three phase line taken through the water phase. $[6]$ Hydrophilic particles are characterized by a value $\theta < 90^\circ$ while large values ($\theta > 90^\circ$) are characteristic of hydrophobic particles. Generally, hydrophilic particles can stabilize O/W emulsions while the opposite holds for hydrophobic particles. $[6]$ We have here no quantitative estimate of how $\theta$ depends on $t_s$. However, we can estimate the value of $t_s$ for obtaining $\theta = 90^\circ$ by another comparison with surfactant stabilized emulsions. When the surfactant is hydrophilically/hydrophobically balanced, the spontaneous curvature of the surfactant loaded interface, $H_0$, is close to zero. $[41]$ Here, emulsions are unstable and coalesce rapidly. $[42]$ It also marks the transition line between O/W to W/O emulsions, $[36]$ for the much studied phase inversion $[43-45]$ of nonionic surfactant stabilized emulsions. The data in Figure 1a demonstrate that the particle properties are shifted from hydrophilic to hydrophobic with increasing $t_s$, and with a transition from O/W to W/O emulsions at $t_s \approx 6h$. It is therefore reasonable that $t_s \approx 6h$ corresponds to $\theta \approx 90^\circ$. Making the analogy between particle contact angle and surfactant film spontaneous curvature has some relevance, but we recall that there are fundamental differences between particle and surfactant stabilized emulsions. In contrast to typical particles, surfactants spontaneously adsorb at the water-oil interface. Furthermore, in surfactant-water-oil systems there are generally equilibrium microemulsion phases, and emulsions are typically supersaturated microemulsions. $[46,47]$

3.2. W/O droplet size

Fixing $\phi_w = 0.2$, and $\phi_p = 0.0032$ we further characterized the W/O emulsions formed after longer soaking times, $t_s$. In Figure 2 we present optical microscope images of emulsions formed after different $t_s$. P1 stabilized-emulsions are shown in Figure 2a, and compared with P2 stabilized-emulsions in Figure 2b. As can be seen in Figure 2a, the droplet size increases monotonically with increasing $t_s$, and thus with the particle hydrophobicity. We estimate the average particle radius, $R$, to be circa 5–10 $\mu$m for $t_s = 0.5$ day, and increases to circa 30 $\mu$m at the longest soaking time, $t_s = 120$ days. Furthermore, a visible excess of particles in the continuous oil phase appears beyond 10 days and grows in quantity after that. As a comparison, the average drop size in the P2 system (Figure 2b) is essentially independent of $t_s$, and excess particles in the oil phase were observed for all soaking times. The average droplet size in the P2 system corresponds approximately to that obtained in the P1 system after $t_s = 60$ days.

Thus, the efficiency of particle adsorption during the emulsification process decreases with increasing
hydrophobicity. From the drop size we can estimate the effective particle concentration, \( \phi_{\text{p,eff}} \), i.e. the volume fraction of particles that are adsorbed at the water-oil interface. Assuming that the adsorbed particles form a hexagonally close packed monolayer, then each particle contribute with an area \( a_p = \pi r_p^2 / 0.91 \). The total interfacial area per unit volume, \( A/V = 3\phi_w / R \). Since we also have \( A/V = 3\phi_{\text{p,eff}} / (4r_p 0.91) \), we finally obtain

\[
\phi_{\text{p,eff}} = 3.64\phi_w \frac{r_p}{R} \tag{1}
\]

With \( r_p = 17 \text{ nm} \), and \( \phi_w = 0.2 \) we obtain that the fraction adsorbed particles \( \phi_{\text{p,eff}} / \phi_p \) decreases from 0.77 for \( t_s = 0.5 \text{ day} \) (\( R \approx 5 \mu \text{m} \)) to 0.13 for \( t_s = 120 \text{ days} \) (\( R \approx 30 \mu \text{m} \)). This trend is consistent with the observation of aggregates of excess non-adsorbed particles in the continuous phase (Figure 2) for longer soaking times.

The reason why \( \phi_{\text{p,eff}} \) decreases with increasing hydrophobicity is not fully clear. However, one possibility is that sonication not only fragments the water domains but also detach particles from the interface, or prevent adsorption, making it not fully covered. Particles are in fact expected to be less strongly anchored at the interface the more \( \delta \) deviates from 90°. If the drops are only partly covered by particles when sonication is terminated, they will coalesce, and coalescence will continue until the interface is completely covered by particles.\(^{[48]}\) During this time there may also be some additional adsorption, depending on the rate of adsorption relative to the rate of coalescence. We expect the adsorption rate to decrease with increasing \( t_s \) as the particles become more and more hydrophobic.

### 3.3. W/O droplet sedimentation

The W/O emulsion droplets sediment. However, because the density difference between the silicon oil and water is small, the sedimentation is relatively slow. To analyze this in more detail, freshly prepared emulsions, with \( \phi_w = 0.20 \) were transferred to 5 mm diameter glass tubes and let to sediment. When the droplets sediment, the supernatant is an essentially pure transparent oil phase and the interphase between the white sediment and the transparent oil phase was sufficiently sharp to assess a sediment height, \( h \). The height of the full sample was always kept constant at \( h_0 = 11 \text{ cm} \). As an example, a sample, stabilized by P2 particles with \( t_s = 120 \text{ days} \), is shown in Figure 3a. The sedimentation was studied by measuring \( h \) as a function of time. In Figure 3b we present the sedimentation profile, where the relative sediment height \( h/h_0 \) is plotted as a function of time. As can be seen, sedimentation occurs on the time scale of hours and a stable sediment height \( h_f \) is obtained at longer times (after circa 5-10 h). In this particular sample, the emulsion is compressed approximately by a factor slightly larger than two, so that \( \phi_w \) is increased to ca. 0.45 in the steady state sediment. Below we will refer to this final volume fraction as \( \phi_f = \phi_w h_0 / h_f \).

Sedimentation curves obtained for emulsions stabilized by P1 and P2 particles with different \( t_s \) are presented in Figure 3c and Figure 3d respectively. For the P1 particle emulsions, both the sedimentation rate and the final volume fraction, \( \phi_f \), depend on the particle soaking time, \( t_s \). For emulsions stabilized by P2 particles, on the other hand, the sedimentation curves are essentially independent of \( t_s \).

![Figure 2. Microscope images of emulsions having \( \phi_w = 0.2 \), prepared with particles having experienced different soaking times \( t_s \). (a) Emulsions prepared with P1 particles. (b) Emulsions prepared with P2 particles.](image)
From the sedimentation curves in Figs. 3c and 3d, the initial sedimentation rate, $v_{in} = \frac{d(h_0/h)}{dt}|_{t=0}$, was evaluated from the initial slopes, as illustrated in Figure 3b, and the results are presented in Figure 4. As can be seen, for P1 particles, $v_{in}$ increases in absolute value with $t_s$ while for P2 particles the rate is essentially independent of $t_s$. This behavior is consistent with the optical microscopy observations (Figure 2) that the emulsion drop size increases with increasing $t_s$ for emulsions stabilized by P1 particles, while for the case of P2 particles the drop size is essentially constant, independent of $t_s$.

The concentration dependence of the sedimentation velocity has experimentally been found to obey\(^{[49]}\):

$$v = \frac{v_0}{1 - \phi_f}^{5.4}$$

[2]

where $v_0$ is the Stokes’ velocity of an isolated drop of radius $R$, given by:

$$v_0 = \frac{2R^2\Delta \rho g}{9\eta}$$

[3]

Here, $\Delta \rho$ is the density difference between the dispersed and the continuous phases, $g$ is the gravitational acceleration constant (9.81 m.s$^{-2}$) and $\eta$ is the solvent viscosity. Knowing that the initial sedimentation rate $v_{in}$ and velocity $v$ are related through: $v = h_0v_{in}$, the average drop radii can be calculated from Equations (2) and (3). The results are plotted in Figure 5a. The average droplet radii obtained from the sedimentation rates, are in reasonable agreement with those estimated from microscopy.

In Figure 5b we have plotted the variation of $\phi_f$ with $t_s$. As can be seen from Figures 3d and 5b, the final water volume fraction in the sediment, $\phi_f \approx 0.45$ is essentially independent of $t_s$ for the P2 stabilized emulsions. On the
contrary, for P1 particles, $\phi_f$ increases from 0.23 to 0.37 with increasing $t_s$. However, in contrast to the variation of $R$, it seems that $\phi_f$ saturates after 90 days of soaking. These values are all significantly smaller than the value for random close packing $\phi_{rcp}$ that should be reached for non-interacting drops. The random close packing depends on the drop size distribution, it is equal to 0.64 for monodisperse spheres higher in the case of polydispersity.\[^{[50]}\]

The low values of $\phi_f$ are likely a consequence of attractive van der Waals interactions between the droplets, resulting in aggregation, and that the sediment is actually a colloidal gel that can support its own weight. Such an observation agrees with the existence of an elastic modulus well below the random close packing as shown by Arditty and co-workers in Pickering emulsions,\[^{[3]}\] or more generally in suspension with weakly attractive particles.\[^{[51]}\]

In the case of a colloidal gel able to withstand its own weight, a stable sediment is expected when the compression yield stress of the network, $P_y$, is equal to the gravitational compression stress, $\sigma_g$, given by

$$\sigma_g = \Delta \rho \phi hg$$  \[4\]

Due to the volume conservation of the dispersed phase, $\phi_s h_0 = \phi_f h_f = \phi(t) h_f(t)$ is constant, meaning that $\sigma_g = 8.6\,\text{Pa}$ is fixed for both systems. $P_y$ varies with radius and concentration approximately as $\phi_c^{[52]}$

$$P_y = A \frac{\phi_f^4}{R^2}$$  \[5\]

although it has been pointed out\[^{[54]}\] that a single power law cannot be expected to describe the concentration dependence over the whole concentration range. Here, $A$ is a constant that depends on the network structure (fractal dimension) and the droplet-droplet interactions. Equation (5) implies that we expect $\phi_f \sim R^{1/2}$. In Figure 6 we have plotted our experimentally determined $\phi_f$ as a function $R$ together with the theoretical prediction $\phi_f \sim R^{1/2}$, shown as a solid line. As can be seen, the data are consistent with the prediction although there is not enough data to accurately verify the scaling exponent. For the P2 system both $R$ and $\phi_f$ are approximately constant. From these data, a rough estimate of $A$ can be given: $A \approx 4 \times 10^{-7}\,\text{N}$ for P1-stabilized emulsions and is of the order of $1 \times 10^{-7}\,\text{N}$ for the system stabilized by P2 particles. The slightly lower $A$-value on the case of P2 particles possibly reflect a lower friction between drops when the particles are hydrophobically modified with the longer PDMS chains.

### 3.4. Centrifugation

Using centrifugation, the emulsions can be further compressed and also be broken at higher rotational speeds. To assess the rigidity of the particle loaded droplet interface, the emulsion samples were centrifuged. The rotational speed was gradually increased, spending 10 minutes at every speed, until the first traces of free water could be detected, as a
sign of emulsion breaking. As previously noted, if the centrifugation times had been increased, a water layer could have been observed for slower rotation speed. Although not performed at equilibrium these experiments allow comparison between the systems. In Figure 7a we present the effective gravitational acceleration, \( \frac{n_g}{C_3} \) (number of g-units) when the first traces of water could be detected, for the different emulsion samples. \( \frac{n_g}{C_3} \) is plotted as a function of the soaking time, \( t_s \), and data are given for both P1 and P2 particle systems. As can be seen, the P1 particle stabilized-emulsions are generally significantly more resistant against compression induced by the centrifugation force, compared to the emulsions stabilized by the P2 particles. However, the P1 system approaches P2 at long soaking time. Again one should notice that the resistance of emulsions depends on the drop size.\(^{[55]}\)

From Figure 7a it appears that the drop sizes of emulsions stabilized by P1 or P2 particles are not significantly different for longer soaking times (\( t_s > 60 \) days), so that the huge difference of resistance at \( t_s = 60 \) days cannot just be explained by a drop size difference.

For some samples in the P1 system we also measured the height of the sediment, from which we can calculate the droplet volume fraction, for the different rotational speeds before breaking of the emulsions. The results are presented in Figure 7b, and the results from the sedimentation experiments at ambient gravitational field, 1 g (Figure 5b), have also been included. As can be seen, with small values of \( n_g \) the emulsions are first compressed to \( \phi = 0.7-0.75 \) that we interpret as the volume fraction of random close packing, \( \phi_{\text{rcp}} \) for the polydisperse emulsions. In this first regime, compaction is easy as we only need to overcome the compression yield stress (initially \( \sigma_y = 8.6 \) N) to induce this dense packing. Increasing further the rotation speed leads only to a minor additional compression, before breakage. This shows that compaction larger than the random close packing is more difficult as it requires drop deformation. Breaking occurs at \( \phi \approx 0.8 \) for all samples, although different \( n_g \) is required. The fact that breaking occurs for a volume fraction so close to \( \phi_{\text{rcp}} \) indicates that the drop interface is rigid but fragile in agreement with other Pickering emulsions.\(^{[3]}\)

Continuous compression beyond close packing results in shape deformations of the initially spherical droplets and a corresponding increase of the interfacial area. Following Princen’s empirical relationship,\(^{[56-58]}\) we have

\[
\frac{\Delta A}{A_0} = 1.093 \left[ 1 - \frac{3.20}{\left( \frac{\phi}{1-\phi} + 7.70 \right)^{1/2}} \right]
\]

where \( \Delta A \) is the area increase and \( A_0 \) is the interfacial area with spherical drops occurring for \( \phi < \phi_{\text{rcp}} \) (neglecting the

---

**Figure 6.** Sediment volume fraction \( \phi_s \), plotted as a function of average drop radius, \( R \), for P1 (red filled circles) and P2 (blue filled triangles) emulsions, respectively. The solid line is a best fit of the relation \( \phi_s = A_R^{1/2} \) to the P1 emulsion data, with A being an adjustable parameter.

**Figure 7.** Compression of sediment by centrifugation. (a, left) The effective acceleration, \( \frac{n_g}{C_3} \) (number of g-units) when the first traces of free water was observed from the sediment, plotted as a function of the particles soaking times, \( t_s \), for P1 (red filled circles) and P2 (blue filled triangles) emulsions, respectively. Insert: Gravitational compression stress, \( \sigma \), at the breaking of the P1 emulsions plotted as a function of \( t_s \). (b, right) Emulsion drop volume fraction in the sediment as a function of the effective gravitational acceleration, \( \frac{n_g}{C_3} \) (number of g-units) for P1 emulsions with different soaking times: \( t_s = 0.5 \) day (red circles), \( t_s = 1 \) day (purple triangles), \( t_s = 10 \) days (blue diamonds), \( t_s = 100 \) days (green diamonds).
interfacial energy, Princen proposed the semi-empirical equation\cite{59,60}

$$\sigma_c = \frac{1.77\gamma}{R} \phi^{1/3} (\phi - \phi_{rcp})$$ \[7\]

allowing us to obtain estimates of $\gamma$.

$$\gamma = \frac{\Delta \rho \phi h n_{gg} R}{1.77\phi^{1/3} (\phi - \phi_{rcp})}$$ \[8\]

As mentioned above, for all the emulsions the limit before breakage is $\phi \approx 0.8$, and we assume $\phi_{rcp} \approx 0.71$. The variation $\gamma$ with $t_s$ is shown as an insert in Figure 7a. As can be seen, rather high values of $\gamma$, 6 N/m, are obtained for intermediate soaking times, 10–60 days. For longer $t_s$ the value decreases, dropping to ca. 0.4N/m for $t_s = 120$ days. For P2 particles, $\gamma$ is close to 0.4N/m independent of $t_s$.

The high effective tension indicates that there are attractive interactions between the particles at the water-oil interface. Attractive interactions are indeed expected when the particle surfaces are heterogeneous.\cite{61-63} Wetting irregularities lead to an undulating contact line and an irregular meniscus leading to a minimum in the particle pair potential as a function of separation. Apart from shape irregularities, the particles may have more or less of hydrophobic and hydrophilic domains. We observe a maximum in the effective $\gamma$ for intermediate soaking times. This may reflect a maximum in the particle heterogeneity. At shorter times the particles are less functionalized and at longer times the approach a homogeneous hydrophobicity. We aim to return to a more quantitative analysis in a forthcoming publication.

### 3.5. Stability of particle functionalization

Until now we have studied the effect of soaking time on the emulsion type and characteristic. We now would like to assess whether hydrophobization, that occurs when particles are dispersed in oil, goes on at the oil-water interface \textit{i.e.} after emulsification. Three possibilities may be considered: i) Hydrophobization continues after emulsification as in the pure oil, ii) the inverse occurs, hydrophobization decreases and particles become again more hydrophilic, or iii) it remains constant, hydrophobization is terminated and irreversible and the contact angle remains constant with no further evolution after emulsification. To discriminate between these scenarios, two experiments were carried out using the P1 particles.

W/O emulsions prepared at $\phi_m = 0.2$ and $t_s = 1$, 10, 30 days (longer $t_s$ were avoided because of the excess particle in the oil phase) were stored at 25°C for a certain period of time called maturing time $t_m$, and was varied in range from 0 to almost 180 days. After that, all samples were sonicated for 5 minutes again and since the initial sedimentation velocity is very sensitive to hydrophobization for P1 particles (see Figure 4), $v_m$ was measured. The effect of $t_m$ on $v_m$ is shown in Figure 8a. As can be seen, the sedimentation velocity does not essentially change with $t_m$ between emulsions which were prepared at same $t_s$. In other words, after the emulsification, the particles keep the functionalization they
acquired during soaking without increasing or losing hydrophobicity.

However, there still is a possibility that the energy input to the system by sonication is too small to cause a re-emulsification of droplets with a change in particle hydrophobicity. For this reason, we destroyed the emulsions and extracted the particles before performing a re-emulsification using these particles (see Figure 8a). W/O emulsions prepared at $\phi_w = 0.2$ and $t_s = 1, 10, 30$ days were kept at 25°C for a maturing time $t_m$ from 0 to almost 60 days as in the previous experiment. After that, all samples were centrifuged and only particles were taken out from the system. By reusing these particles, emulsions at $\phi_w = 0.2$ were prepared immediately in order to maintain $t_s$ and $t_m$ at their previous values (no additional time neither for $t_s$ nor for $t_m$). Emulsions formed were of the W/O type for all particles and $\nu_{on}$ is plotted in Figure 8b. The initial sedimentation velocities do not change with $t_m$ and are similar to the ones measured with non destroyed emulsions that were just re-sonicated (Figure 8a). In addition, we prepared an O/W emulsion by using particle P1 at $\phi_w = 0.8$ (see Figure 1) and $t_s = 0$ and kept this emulsion for $t_m = 90$ days at 25°C. Then particles were taken out from the emulsion after breaking it by centrifugation and we used these particles for emulsification at $\phi_w = 0.2$. The resulting emulsion is of type O/W. From these results, we conclude that hydrophobization of particles progresses only in the pure oil. The process is apparently inhibited by the presence of water. However, the functionalization is irreversible and the contact angle acquired before emulsification remains constant in the emulsion.

3.6. Effect of temperature

Finally, to assess the effect of temperature on hydrophobization kinetics, soaking of P1 particles were also performed at 80°C. After soaking for a time $t_s$, the oil containing particles were cooled to room temperature and emulsions at $\phi_w = 0.2$ were then prepared following the same procedure as previously. We can assess the effect of temperature by comparing the soaking time needed to invert the emulsion from the initial O/W to W/O. For soaking at room temperature this time is 6 hour. For soaking at 80°C, this time is reduced to ca. 1 hour. We thus conclude that hydrophobization is accelerated when increasing the temperature.

4. Conclusions

We have demonstrated that silica coated titania particles may be hydrophobically modified/functionialized by letting the particles soak in a cyclic PDMS oil. The contact angle at the water-oil interface can be conveniently tuned by simply adjusting the soaking time. The functionalization is terminated when water is added and the sample emulsified. It is irreversible, i.e. it cannot be removed by washing. The kinetics of functionalization is accelerated upon increasing the temperature.

The average drop size of W/O emulsions increases with increasing particle hydrophobicity because of a decreasing affinity for the interface as the particles become increasingly hydrophobic. The emulsions sediment and the water volume fraction, $\phi_w$, in the sediment that settles in the ambient gravitational field, varies approximately as $R^{1/2}$, consistent with theory. Increasing the compressional stress, $\sigma_c$, by centrifugation first concentrates the sediment for small values of $\sigma_c$ up to $\phi_w = 0.7$–0.75. Increasing $\sigma_c$ further eventually result in breaking of the emulsions. From analyzing the $\sigma_c$ values at breaking we estimate an effective interfacial tension, $\gamma$, of the particle loaded water-oil interface. Obtained values are in the range 0.6 – 6 N/m, with a maximum at intermediate particle hydrophobicity. We attribute the high tensions to attractive interactions between the particles that possibly form an essentially condensed layer with significant cohesive forces at the water-oil interface. Attractive interactions are indeed expected for patchy or inhomogeneous particle surfaces. The maximum in $\gamma$ is possibly related to that the particles are maximally inhomogeneous at intermediate functionalization.

It may be useful to study this type of particle functionalization and corresponding emulsion properties using model spherical, well controlled Stöber silica particles.[64] While the chemistry behind the observed functionalization remains unclear, soaking particles in silicone oil is a simple and convenient way for tuning the particles' wettability allowing stabilization of either oil-in-water or water-in-oil Pickering emulsions with the same initial particles. Such a fast and easy method for particle functionalization should open the field to numerous applications.

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