Evolution of Equilibrium Pickering Emulsions—A Matter of Time Scales

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A new class of equilibrium solid-stabilized oil-in-water emulsions harbors a competition of two processes on disparate time scales that affect the equilibrium droplet size in opposing ways. The aim of this work is to elucidate the molecular origins of these two time scales and demonstrate their effects on the evolution of the emulsion droplet size. First, spontaneous emulsification into particle-covered droplets occurs through *in situ* generation of surface-active molecules by hydrolysis of molecules of the oil phase. We show that surface tensions of the oil—water interfaces in the absence of stabilizing colloidal particles are connected to the concentration of these surface-active molecules, and hence also to the equilibrium droplet size in the presence of colloids. As a consequence, the hydrolysis process sets the time scale of formation of these solid-stabilized emulsions. A second time scale is governing the ultimate fate of the solid-stabilized equilibrium emulsions: by condensation of the *in situ* generated amphiphilic molecules onto the colloidal particles, their wetting properties change, leading to a gradual transfer from the aqueous to the oil phase via growth of the emulsion droplets. This migration is observed macroscopically by a color change of the water and oil phases, as well as by electron microscopy after polymerization of the oil phase in a phase separated sample. Surprisingly, the relative oil volume sets the time scale of particle transfer. Phase separation into an aqueous phase and an oil phase containing colloidal particles is influenced by sedimentation of the emulsion droplets. The two processes of formation of surface-active molecules through hydrolysis and condensation thereof on the colloidal surface have an opposite influence on the droplet size. By their interplay, a dynamic equilibrium is created where the droplet size always adjusts to the thermodynamically stable state.

Introduction

Two classes of emulsions are known to exhibit thermodynamic stability at present: microemulsions[1] and a special class of Pickering emulsions.[2,3] Their equilibrium state is determined by the volume fractions of the basic components, oil and aqueous phase, the type and amount of stabilizer, the temperature, and the pH. For stabilization surfactants, cosurfactants, solid particles, salt, and combinations thereof may be employed. Thermodynamic stability in microemulsions is provided by very low interfacial tensions created by adsorption of surfactants and possibly cosurfactants at the oil—water interface.[1] In the only recently discovered special class of Pickering emulsions,[2] a combination of interfacial tensions of the bare oil—water interface below ~10 mN/m, stabilizing colloids smaller than 200 nm, and amphiphilic ions leads to thermodynamic stability.[2,3] A systematic study of this system is described in detail in a previous publication; see ref 3. The term Pickering emulsion generally refers to solid stabilized emulsions that were first discovered by Pickering and Ramsden at the beginning of the 20th century.[4,5] Notably, apart from the system we focus on in this Article, all other Pickering emulsions are only of kinetic and not thermodynamic stability.[6] To make the distinction between common, metastable Pickering emulsions and the special type of thermodynamically stable Pickering emulsions investigated here, the thermodynamically stable emulsions are also sometimes termed solid-stabilized equilibrium emulsions.[3]

In contrast to other oil—water systems which require significant energy input for their formation, for example, by mechanical mixing, thermodynamically stable emulsions form spontaneously upon mixing of the components. Their final state, such as the droplet size or whether an oil-in-water or a water-in-oil emulsion is formed, is determined only by the concentrations of the components and the type of emulsifiers added. In solid-stabilized equilibrium emulsions, for example, the droplet size in the absence of an excess oil phase increases roughly linearly with the oil—colloid mass ratio.[2] Mixing two emulsions with different average droplet sizes results in an intermediate droplet size.[2] Generally, when mixing two emulsions that are thermodynamically stable, the intermediate state is obtained corresponding to the new concentrations of the components. This also implies that the order of mixing of the constituents does not affect the state of the emulsion.

Not only deliberate changes in the composition may induce an adaptation of the emulsion system to the new conditions, but also chemical processes, though unreported as of yet, should trigger a spontaneous response and alter the state of the emulsion. Here, we report on thermodynamically stable Pickering emulsions in which a slow chemical change competes with the generally much faster formation of the solid-stabilized emulsion. The primary goal of this Article is to explain the observed changes in the emulsion droplet size by the underlying molecular processes. We first investigate the role that in situ generation of surface-active molecules plays on spontaneous emulsion formation. Then, we explore the reasons that lead to emulsion droplet size growth. Intriguingly, these competing time scales govern the evolution of the emulsion droplet size. We

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find that the droplet size always adapts to the lowest free energy state as defined by the emulsion conditions, leading to a dynamic equilibrium.

Materials and Methods

A. Colloidal Dispersions. Colloidal magnetite dispersions (Fe_3O_4) were prepared following a precipitation method described by Massart.[7] 40 mL of a 1 M aqueous solution of $FeCl_3$ and 10 mL of an acidic (2 M HCl) aqueous solution of 2 M $FeCl_2$ were combined and added to 500 mL of 0.7 M NH_4OH under vigorous stirring. The immediately precipitated black magnetite was collected with a magnet, decanted, and redispersed overnight in 50 mL of a 1 M solution of tetramethylammonium hydroxide (TMAH). The magnetite particles were then transferred to Millipore water via magnetic decantation. The final dispersion contained nonaggregated, negatively charged magnetite colloids with an average diameter of $11 \pm 28\%$ nm.

Similarly, aqueous dispersions of cobalt ferrite ($CoFe_2O_4$) nanoparticles of $20 \pm 27\%$ nm were prepared by the coprecipitation of iron chloride and cobalt chloride salts.[8,9] First, 2.38 g (0.01 mol) of $CoCl_2 \cdot 6H_2O$ was dissolved in a solution of 1 mL of HCl (37%) in 4 mL of water and 5.406 g (0.02 mol) of $FeCl_3 \cdot 6H_2O$ was dissolved in 40 mL of water. These solutions were both heated to 50 °C, subsequently mixed, and quickly added to a 200 mL solution of boiling 1.0 M aqueous NaOH under vigorous stirring. After stirring for 30 min at 100 °C, the black mixture was cooled down to room temperature. The particles precipitated within minutes and were collected with a magnet, the supernatant was decanted, and the black sediment was redispersed in 100 mL of H_2O. This procedure was used to rinse the particles four times with 100 mL of H_2O. The resulting sediment was redispersed in 30 mL of 2.0 M HNO_3 and stirred for 5 min, upon which 30 mL of 0.35 M $Fe(NO_3)_3 \cdot 9H_2O$ was added. The reaction mixture was refluxed for 45 min, after which it was cooled down to room temperature. After sedimentation of the particles with a magnet and removal of the supernatant, they were redispersed in 50 mL of 1 M tetramethylammonium hydroxide (TMAH) overnight under stirring. Finally, the particles were sedimented on a magnet to remove the excess of TMAH and redispersed in approximately 60 mL of H_2O.

Ludox AS-40 silica dispersions (DuPont) containing 50% w/w amorphous colloidal silica with a diameter of $25 \pm 18\%$ nm in an aqueous ammonium hydroxide solution were diluted with Millipore water to 10.36% w/w. 100 mL of this silica dispersion was dialyzed for 5 days during which the dialysate (water) was exchanged four times. After filtration through 0.2 μm Millipore filters and further dilution, an aqueous dispersion of 2.85% w/w nonaggregated silica was obtained. After transfer to Millipore water, the dispersion was prepared at volume fractions of 1.0% w/w.

B. Emulsion Preparation. *General Procedure for Emulsion Preparation.* The components were added in no specific order, as the final state of a thermodynamically stable system only depends on the relative amounts of the components and not on the sequence of addition. Colloidal suspensions were diluted with Millipore water to the mentioned weight fractions. The oil phase consists, unless stated otherwise, of (3-methacryloxypropyl) trimethoxysilane (TPM, Acros Organics, used as received, stored at 4 °C), a polymerizable trialkoxysilane that can form surface-active molecules through hydrolysis and dissociation of weakly acidic silanol groups. After preparation, the samples were stored on a vibration-free table in a dark, temperature-controlled room.

Polymerization. Polymerization of the particle-stabilized TPM droplets was achieved by addition of potassium persulfate (0.5 mL of 23 mg/mL aqueous potassium persulfate (KPS) per 3 mL of emulsion) at 70 °C for 10 h.

Stability at High TPM Concentrations. A series of magnetite-stabilized TPM emulsions was prepared to investigate the emulsion stability at high oil concentrations. Each sample contained 2.0 g of a 0.125% w/w magnetite dispersion and different TPM volumes, such that the corresponding mass ratios $m_{TPM}/m_{Colloid}$ were 100, 150, 200, 250, 300, 350, 400, 500, 600, and 1000. The samples were gently homogenized several times a day during the first three days to separate emulsion stability from effects due to sedimentation. Furthermore, three samples containing 2.0 g of a 0.125% w/w magnetite dispersion with mass ratios $m_{TPM}/m_{Colloid}$ of 160, 240, and 400 were prepared. These samples were not shaken during the observation.

Long Time Emulsion Stability. Two emulsions were prepared by the addition of 0.104 and 0.466 g of TPM to 44.45 and 42.17 g of 1.2 g/L cobalt ferrite dispersions in water, to obtain oil–colloid weight ratios $m_{TPM}/m_{Colloid}$ of 2.0 and 9.2, respectively. The emulsions were monitored for 20 days by visual observation, and aliquots of 1.5 mL were taken and polymerized for investigation by TEM. The emulsion was homogenized by shaking before a sample was taken.

(3-Methacryloxypropyl) Triethoxysilane. We used (3-methacryloxypropyl) triethoxysilane (MPTES, used as received from ABCR), an oil with a chemical structure equivalent to TPM but with three ethoxy groups instead of three methoxy groups attached to the silane moieties. The ethoxy groups of the oil are more resistant to hydrolysis, while MPTES still has a chemical structure similar to TPM. From these experiments, the influence of the surface-active molecules generated through hydrolysis on thermodynamic stability can be determined. Besides using pure MPTES in the oil phase, we also prepared emulsions with different ratios of TPM and MPTES at a fixed oil–colloid weight ratio of 5. For each sample, we added 0.11 g of oil to 10.5 g of a 0.2% w/w magnetite dispersion. By doing so, we investigated whether fractions of TPM in the oil phase provide sufficient surface-active molecules to induce stability.

C. Characterization. *Electron Microscopy.* Polymerized emulsion droplets were imaged by transmission electron microscopy (TEM, TECNAI 10 or TECNAI 12, Philips). Samples were prepared by drying drops of diluted dispersions on polymer coated copper TEM grids. Polymerized sediment was sputter coated with platinum/paladium prior to imaging by scanning electron microscopy (SEM XL FEG 30).

Dynamic Light Scattering (DLS). Dynamic light scattering was performed on diluted emulsions at 25 °C using an argon ion laser ($\lambda = 641.7$ nm, 400 mW, Spectra Physics). Samples were diluted immediately before measurement to minimize any effect of dilution on the thermodynamic state of the emulsion.

Interfacial Tension. The surface tensions of various oils embedded in a 6 mM aqueous TMAH phase were determined at 25 °C using a spinning-drop tensiometer.[10] The samples were prepared by first filling glass tubes with the denser phase, after which droplets of the lighter phase were injected. Mixtures of MPTES and TPM at 70/30, 50/50, and 30/70 with densities close to 1 g/cm³ were measured against an aqueous phase containing 75% w/w D_2O (density of the mixture 1.08 g/cm³). For mixtures of 10/90 TPM/MPTES, 50% D_2O was used in the aqueous phase to obtain a density of 1.05 g/cm³. The angular velocity of the spinning tube was measured using an optical sensor. The droplet size was measured by observation through a microscope. The surface tension was determined from the droplet deformation
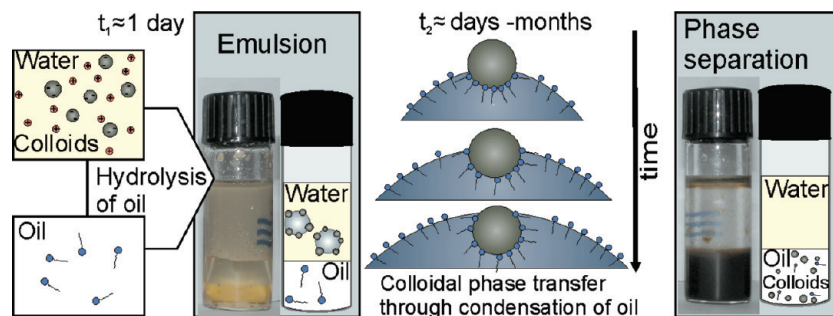
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Figure 1. Schematic drawing of the two processes of hydrolysis and condensation occurring in the emulsion system. Hydrolysis leads to spontaneous emulsification on the time scale of a day. Gradual coating of the colloidal particles by condensation of hydrolyzed oil molecules transfers them to the oil phase, with phase separation as the final state.

in the centrifugal field as a function of the rotational speed, using the Vonnegut equation:[10] $\gamma = \Delta\rho\omega^2 r^3/4$, which is valid if $l > 4r$. Here, $\Delta\rho$ is the density difference between the heavy and the light phase, r is the droplet radius perpendicular to the axis of rotation, and l is the droplet length along the axis of rotation.

Results and Discussion

Upon mixing of aqueous colloidal suspensions and a particular oil, (3-methacryloxypropyl) trimethoxysilane (TPM), emulsification into monodisperse oil droplets covered with colloidal particles is observed. Direct evidence for this spontaneous emulsification was provided by confocal microscopy of water and TPM containing fluorescent dye.[11] In the absence of colloidal particles, oil droplets undergo coarsening, whereas in the presence of magnetite colloids the oil droplets shrink in size. Within 2 h, a large fraction of TPM is dispersed into droplets covered by solid particles. Chain formation of the droplets in a magnetic field confirms that the magnetite colloids are adsorbed onto the droplet interface. Ludox silica stabilized emulsions are forming on the time scale of 2 days, as indicated by the angle-independent size measured by dynamic light scattering (DLS).[11] Other stabilizing colloidal particles, such as Bindzil silica, cobalt ferrite, and gold also induce emulsification within a day.[3,11]

The time scale for the formation of these solid-stabilized emulsions is linked to the time scale of partial hydrolysis and subsequent dissociation of the TPM molecules in the oil phase (Figure 1). The dissociated hydrolyzed TPM molecules are amphiphilic and hence adsorb at the oil−water interface, lowering the interfacial tension.[3,12] In the presence of 6 mM aqueous tetramethyl ammonium hydroxide (TMAH), the interfacial tension continuously decreases from 8 to 3 mN/m over the course of 24 h.[12] Therefore, using an oil with the much less readily hydrolyzing ethoxy[13] instead of methoxy groups, (3-methacryloxypropyl) triethoxysilane (MPTES), does not yield emulsification within a few days. The interfacial tension between MPTES and 6 mM aqueous TMAH is 17 mN/m immediately after mixing (Table S1, Supporting Information), too high for spontaneous emulsification in the presence of colloidal particles.[3] Within 24 h, the interfacial tension decreases down to 7 mN/m, even though no stable emulsions are obtained on that time scale. Emulsification occurs 1 week after mixing of the components, which is in line with the 6−10 times longer time scale of hydrolysis.[13]

Mixtures of MPTES and TPM have interfacial tensions in between the values of pure TPM and pure MPTES (Figure 2A, Table S1, Supporting Information). This indicates that the oils mix on the molecular level with compositions of TPM and
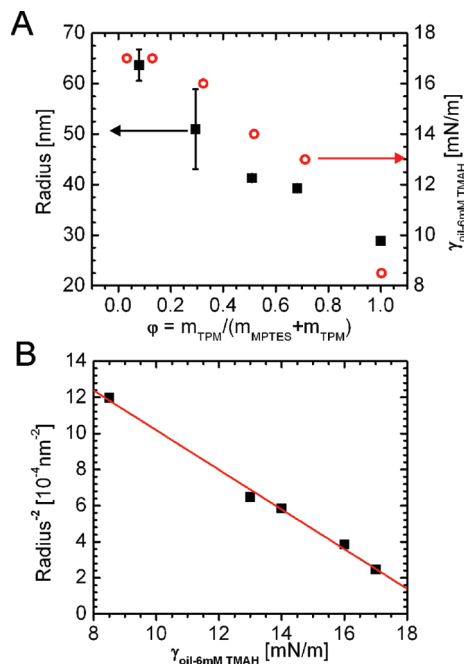

Figure 2. Emulsions containing magnetite particles and an oil phase consisting of MPTES and TPM show a correlation between surface tension of the bare oil−water interface and emulsion droplet size. No excess oil phase was present in these samples. (A) Radii of emulsion droplets measured by dynamic light scattering (DLS) as a function of the relative amount of TPM in the oil phase (left) and surface tension of TPM−MPTES mixtures against 6 mM aqueous TMAH as measured by spinning drop tensiometry in the absence of colloidal particles (right). (B) The inverse droplet size scales quadratically with the surface tension of the bare oil−water interface (fit: $R^{-2} = 2.12 \times 10^{15}$ m^{-2} − 1.10×10^{17} J$^{-1}\gamma_{\text{ow}}$).

MPTES on the droplet surface equaling the bulk composition. For an oil phase comprised of a mixture of MPTES and TPM, spontaneous emulsification occurs at all volume ratios in the presence of TMAH stabilized magnetite colloids. DLS measurements 5 days after mixing show that the droplet radius decreases with an increasing percentage of TPM in the oil phase, $\varphi = m_{\text{TPM}}/(m_{\text{TPM}} + m_{\text{MPTES}})$ (see Figure 2). The sample with the smallest fraction of TPM, $\varphi = 0.08$, was measured again 15 days after mixing. The droplet size slightly decreased over this period of 10 days from 64 ± 2 to 59 ± 1 nm. This decrease in droplet size might be due to the onset of the slower partial hydrolysis of MPTES.

The droplet size and surface tension measurements on TPM−MPTES mixtures further support the hypothesis that the hydrolyzed fraction of TPM molecules forms surface-active molecules that consecutively occupy the droplet surface. The larger the fraction of TPM in the bulk oil phase, the more

hydrolyzed TPM molecules are generated and the lower the surface tension of the bare oil−water interface is. Hence, more interface between oil and water can be created and the droplets shrink. Fitting the data presented in Figure 2B, we find a linear relation between the inverse square of the radius and the bare oil−water interfacial tension, $R^{-2} = 2.12 \times 10^{15}$ m^{-2} − 1.10×10^{17} J$^{-1}\gamma_{ow}$. This indicates, indeed, that more total droplet surface area, which scales with R^2, can be created when the interfacial tension between the oil and water phase is lower.

The contribution of the bare oil−water interface to the formation energy of one droplet would be $4\pi R^2(1 - s)\gamma_{ow}$, where R is the radius of the droplet, s is the fraction of the droplet surface covered with colloidal particles, and γ_{ow} is the surface tension of the bare oil−water interface. Filling in typical values for such an emulsion, $R = 30$ nm, $s = 0.7$, and $\gamma_{ow} = 10$ mN/m, the energy per droplet would be on the order of 10^5 k_BT—way larger than the thermal energy which should be the dominating energy scale. Therefore, we conclude that the surface tension of the emulsion interface in the presence of colloidal particles, surface-active TPM molecules, and surface-active quaternary ammonium ions is orders of magnitude lower than that between TPM and aqueous TMAH only. Preliminary surface tension measurements on an aqueous droplet containing magnetite stabilized emulsions against TPM confirmed significantly lower surface tensions. We conjecture a collective effect between the colloidal particles, surface-active molecules, and ions in analogy to microemulsions.[3]

After formation, the equilibrium Pickering emulsions can remain stable for days to months, with the time scale of stability depending on the specific composition of the emulsion. Macroscopically, a change in the droplet size can be noticed by the color of the emulsions turning lighter, manifesting larger light scattering objects and thus growth of the emulsion droplets. An emulsion consisting of TPM and cobalt ferrite colloids at an oil−colloid weight ratio $m_{TPM}/m_{Colloid}$ of 2 turns from black/gray to gray/brown within 20 days (Figure S2, Supporting Information). From TEM images of polymerized aliquots of this emulsion, we quantified the size increase in time. Over the course of 20 days, the size of these emulsion droplets increases roughly from 50 to 90 nm, whereas polydispersity increases only slightly (see Figure 3A). TEM images after 2 and after 15 days show that the size of the droplets increased while the effective surface area per colloid decreases from 3.2×10^3 nm^2 after 2 days to 2.3×10^3 nm^2 after 20 days (Figure 3B,C). In other words, the colloidal particles are more closely packed at the interface after 20 than after 2 days. This denser surface occupation implies that the charge of the colloidal particles has decreased, allowing for closer approach which in turn leads to droplet growth because the colloidal particles can stabilize less oil−water surface area. If this droplet size increase would be due to Ostwald ripening,[14,15] the radius should scale as $r \propto t^{1/3}$. Fitting the experimental data with $r = a \cdot t^b$ yields $a = 44$ nm and $b = 0.25 \pm 0.02$, which makes Ostwald ripening not likely to be the mechanism for the size increase. We have observed droplet growth in time in various solid-stabilized equilibrium emulsions. Also, for a cobalt ferrite stabilized TPM emulsion with an oil−colloid weight ratio of $m_{TPM}/m_{Colloid} = 9$, that is in the presence of an excess phase, the average droplet diameter increased from 80 ± 15 to 191 ± 73 nm over the course of 2 weeks.

Eventually, the emulsions become unstable and form brown sediment. By polymerizing a magnetite as well as a cobalt ferrite emulsion that had been allowed to settle to the bottom of the flask, we could image the sediment with scanning electron
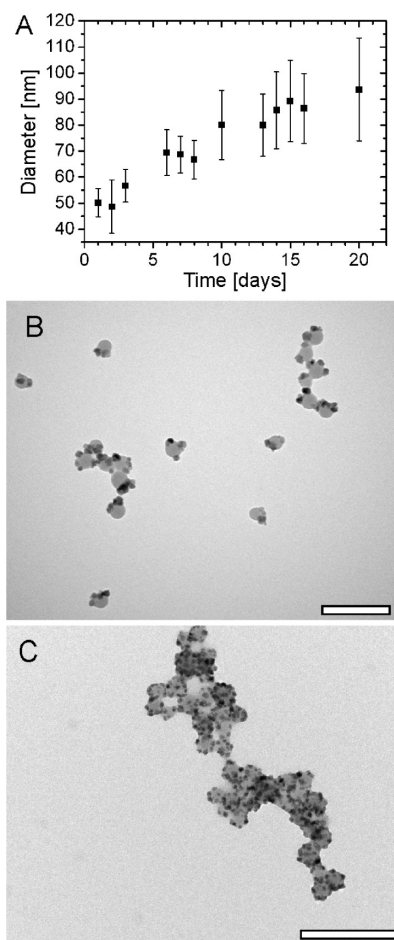

Figure 3. (A) Diameter of cobalt ferrite stabilized TPM emulsion droplets as measured from TEM images of polymerized samples. Over the course of 20 days, the emulsion droplet size grows linearly up to double the diameter without a significant increase in polydispersity. TEM images of polymerized aliquots after (B) 2 days (scale bar is 200 nm) and (C) 15 days (scale bar is 500 nm).

microscopy (SEM). The sediment consists of a continuous phase with attached and partly coalesced droplets, as can be seen in Figure 4. Droplets and continuous phase are covered with magnetite colloids. The color of the macroscopic sediment was identical to that of the colloidal suspension, whereas the supernatant became fully transparent. Similar experiments with cobalt ferrite colloids lead to comparable observations.

The time scale of sedimentation and coalescence, and ultimately transfer of magnetite to the oil phase, is linked to the relative amounts of oil and colloidal particles. To illustrate this dependence, we prepared a series of magnetite stabilized TPM emulsions with oil−colloid mass ratios ranging from 100 to 1000 and observed the transfer macroscopically in time (Figure 5, Figure S1, Supporting Information). All samples contained an equal volume of a 0.125% w/w magnetite colloidal suspension yet different volumes of TPM. Ten h after preparation of the samples, all flasks exhibit two distinguishable phases: an aqueous upper phase consisting of colloid stabilized oil droplets and an excess oil phase on the bottom of the sample flask. The oil phase of samples with mass ratio $m_{TPM}/m_{Colloid} = 400$ and above appears slightly brownish, whereas samples below 400 exhibit a transparent oil phase. Since TPM by itself is a colorless liquid, the brown color of the oil phase indicates the presence of magnetite colloids. This is corroborated further by the response of the emulsion and excess phase to the presence of a magnet. After 2 days, the bottom phase of the sample with
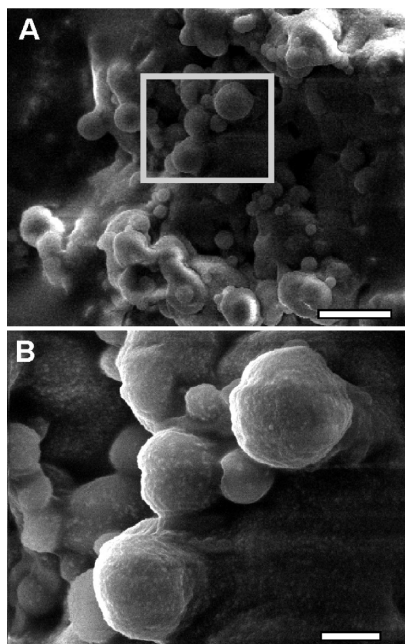
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Figure 4. SEM micrographs of polymerized sediment of a magnetite stabilized TPM emulsion. (A) A continuous phase with attached and partly coalesced droplets is visible (scale bar is 2 μm). (B) Magnified image of the rectangle in part A: the surface is covered with magnetite colloids (scale bar is 500 nm).
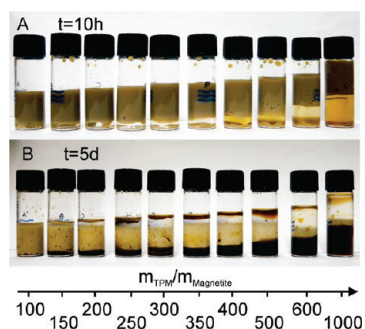

Figure 5. Emulsions containing magnetite colloidal particles and increasing volumes of TPM in the presence of an excess oil phase. (A) After 10 h, emulsification of the aqueous (top) phase is indicated by increased turbidity. Samples above a TPM−magnetite mass ratio of 400 already show coloring of the bottom (TPM) phase due to migration of magnetite. (B) After 5 days, most of the magnetite particles have transferred to the bottom phase, indicated by the brown color. In the upper phase, emulsion droplets sediment with a sharp interface. Sedimentation occurs faster the larger the relative oil volume is.

an oil−colloid mass ratio of 250 does not yet strongly respond to the magnet, whereas the sample with an oil−magnetite mass ratio of 500 does (Figure 6A and B, respectively). After 5 days, the transfer of magnetite particles has proceeded to the point that the oil phase of all samples has turned brown/black and is magnetically responsive (Figures 5B and 6D). Note that, before particle migration, the magnet attracts the magnetite stabilized emulsion phase more strongly (Figure 6C). Homogenization of the system by gentle shaking several times a day does not influence the relative time scales of particle transfer: the colloids migrate more quickly to the oil phase with higher relative oil volumes (Figure S3, Supporting Information). However, the regularly mixed samples show with increasing oil volume a less abrupt transition between an emulsified and a phase separated state than the undisturbed samples. Possibly this difference originates from sedimentation of the emulsion droplets to the excess oil phase, which is prohibited by shaking. Furthermore,
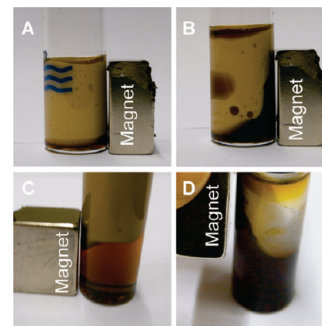

Figure 6. Two days after preparation emulsions with (A) an oil−magnetite mass fraction of 250 do not show significant attraction of the bottom phase to the magnet, whereas (B) the dark brown oil phase of an emulsion with an oil−magnetite mass ratio of 500 strongly reacts to the magnet. (C) Before migration, the magnetite stabilized aqueous emulsion phase gets attracted more strongly to the magnet than the oil phase ($m_{TPM}/m_{Colloid} = 1000$). (D) After phase separation (5 days), the oil phase is strongly magnetic.

the overall magnetite migration took place faster for the gently homogenized samples. Shaking not only prevents sedimentation of the droplets to the interface but also alleviates diffusion limitations within the aqueous phase, for example, for dissolved TPM molecules, and may increase the oil surface exposed to the aqueous phase, leading to more hydrolyzed TPM molecules.

For much smaller relative oil volumes, the time scale of particle transfer lengthens significantly. Magnetite emulsions have been reported to be stable for months,[2] and the cobalt ferrite stabilized TPM emulsion with oil−colloid mass ratio of 2 (Figure 3A) still exhibits emulsion droplets with a uniform size after 20 days (Figure 3C). For cobalt ferrite emulsions with an oil−colloid mass ratio of 9 (Figure S2, Supporting Information), phase transfer has completed after 20 days, as indicated by the black sediment on the bottom of the flask. The gradual emergence of the magnetic feature of the TPM phase at different times in the samples again demonstrates the oil volume dependent time scale of colloidal migration to the oil phase.

The colloidal transfer from the aqueous to the oil phase is not restricted to magnetite or cobalt ferrite stabilized TPM emulsions but was also observed for Ludox silica particles in combination with TPM, as well as magnetite colloids in combination with fatty acids.[16] The latter are currently under investigation with respect to their similarities with TPM emulsions. In all cases, the transfer from the aqueous to the oil phase was observed to be faster with a higher relative oil volume.

The migration of colloidal particles to TPM likely occurs because of a slow condensation of hydrolyzed TPM molecules on the colloidal surface, rendering the colloids gradually more hydrophobic over the course of time. Silica particles deliberately coated with TPM support this scenario: the colloids were found to be stable in organic solvents yet less stable in weakly polar organic solvents and unstable in water.[17] Self-condensation of alkoxysilanes is known to happen on oxides of iron, such as magnetite, and certainly is expected for silica surfaces.[17−19] Indications for this condensation reaction were found in infrared absorbance spectra on colloidal magnetite that was removed from a stable TPM emulsion by washing with ethanol.[20] Infrared absorbance spectra show a strong absorbance peak typical for TPM, indicating that TPM is still present on the magnetite surface. Furthermore, colloidal magnetite in ethanol as well as in TPM forms a stable dispersion, suggesting steric stabilization by the adsorbed TPM. The time scale governing the emulsion droplet growth therefore is comparable to the one governing
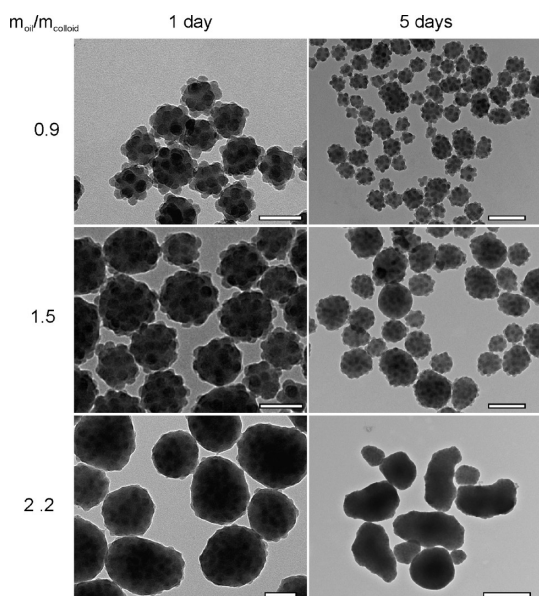
Figure 7. TEM micrographs of Ludox silica stabilized TPM emulsions at different oil−colloid concentrations ($m_{oil}/m_{colloid}$ from 0.9 to 2.2 top to bottom, no excess oil phase) and polymerized 1 and 5 days after mixing the components (scale bars: left side 100 nm, right side top to bottom 200, 200, and 500 nm).

the condensation of TPM on the colloidal particles. The time scale of condensation is set by various factors, such as temperature and pH.[18,21] If the coating renders the colloidal particle sufficiently hydrophobic, the particle migrates to the oil phase (see Figure 1 for a schematic drawing). Therefore, the eventual phase separation into a transparent aqueous and an oil phase containing colloidal particles is a consequence of particle transfer to TPM.

Nevertheless, it is surprising that the migration of colloidal particles is faster with increasing relative oil volume. A likely scenario for explaining this behavior is that the number of hydrolyzed TPM molecules is higher for larger relative oil volumes, for example, due to more oil−water interfacial contact or dissolution of water molecules in the oil phase. If more hydrolyzed TPM molecules are dissolved in the aqueous phase, faster coverage of the colloidal surface and therefore transfer to the oil phase is expected.

The volume dependent time scale of particle coating has another surprising consequence: in the magnetite stabilized TPM emulsions with large excess oil phase, sedimentation of the emulsion droplets of the aqueous upper phase occurs with a sharp interface between the transparent aqueous phase and the turbid light brown emulsion phase. The larger the relative oil volume, the faster the emulsion sediments, and hence the larger the emulsion droplets must be. This observation is surprising, because the solid-stabilized emulsions, in analogy with the preferred curvature of microemulsions, are expected to have a constant droplet size in the presence of an excess oil phase, independent of the volume thereof.[2,22] However, through faster condensation of TPM on the particle surface, the charge on the colloidal particles decreases,[23] relieving the charge induced bending of the interface and leading to a lower preferred curvature of the droplets. Therefore, the emulsion droplets grow despite the presence of an excess oil phase with an increasing oil volume.

Also, in the absence of an excess oil phase, the coating with TPM leads to droplet growth in time (Figures 3 and 7). Here, it is not a preferred curvature that determines the droplet size,

because of a shortage of oil volume. The radius of the droplets is given by the total oil volume, V_{oil}, and surface, A_{tot}, as $R = 3V_{oil}/A_{tot} = 3V_{oil}/(\sigma_{col}N_{col})$. From this relationship, droplet growth in time can be explained by either a decrease in the number of colloidal particles at the interface, N_{col}, or the effective surface area per colloid, σ_{col}. For cobalt ferrite stabilized emulsions, the droplet radius slowly increases while the effective surface area of the colloidal particles continuously decreases in time, as mentioned earlier (Figure 3A). From the TEM images, we deduce that it is rather a lowering of the colloidal charge by coating with TPM that induces an effectively smaller area per colloidal particle than transfer of whole particles to the oil phase that accounts for the droplet growth.

One of the consequences of the gradual coating of the stabilizing colloidal particles with TPM is that the wetting angle between the colloids and the aqueous and the oil phase continuously changes in time. This can best be seen in Ludox silica stabilized TPM emulsions, where the change of the wetting angle occurs both with the available oil volume and with time, though the electron microscope images allow for a rough characterization only (Figure 7). At an oil−colloid ratio of 0.9, the silica particles have a wetting angle smaller than 90° (measured through the aqueous phase) which increases to values above 90° for an oil−colloid ratio of 2.2, and possibly even 180°. Four days later, TEM micrographs show furthermore that the droplets have grown in size and that the droplet shape is less uniformly spherical. The first observation can only partially be explained by a decrease in the colloidal charge by coating with TPM, because the colloids were already closely packed 1 day after emulsion preparation. We conclude that in this case it is not the effective interface per colloidal particle that decreases but rather the number of stabilizing particles adsorbed at the droplet interface. After 5 days, a fraction of the silica colloids is fully immersed in the oil droplets, leading to less total available surface area and droplet growth as a consequence. The droplet deformation could be due to an inhomogeneous distribution of wetting angles or a more rigid oil surface due to self-condensation of TPM.

From our observations on droplet size growth and chemical changes leading to different wetting properties of the stabilizing particles, the thermodynamic stability of the Pickering emulsions may come into question. However, there are convincing experiments that demonstrate thermodynamic stability and point to a more intricate equilibrium: spontaneous emulsification occurs only in the presence of colloidal particles,[3] and reproducibly leads to a specific droplet size depending on the oil volume relative to the number of colloidal particles.[2] Even more so, an intermediate droplet size is obtained from mixing two emulsions with a different equilibrium droplet size.[2] Also, the order of addition of the constituents does not influence the outcome. These observations strongly suggest that a thermodynamic equilibrium exists toward which the system develops depending on the total amounts of the components.

Along that line, we consider this system to be thermodynamically stable, despite the slow chemical changes taking place over time. By definition, thermodynamic equilibrium exists if changes in an equilibrated system are much slower than an experimental observation time. The slow process here is formation and condensation of surface-active molecules onto the particle surfaces. This changes the particle wetting properties, and the system moves to a new equilibrium state. If another oil−colloid system is found that does not rely on *in situ* generation of surfactants that can condense on the particle surface, the change in the wetting properties of the colloids due to the chemical

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processes of hydrolysis and condensation will be prevented. In the presented oil−colloid system, the emulsion adapts to the change in the wetting properties of the colloids. However, it does so in a controlled way; that is, the droplets collectively grow in size without becoming polydisperse. The latter suggests a minimum in the free energy, which determines the state toward which the emulsion evolves. Hence, the presented type of stable Pickering emulsions exhibits an intricate equilibrium emulsion whose formation and evolution depends on two time scales that are linked to the chemical processes hydrolysis and condensation of the oil molecules.

Conclusions and Outlook

Intriguingly, the solid particle stabilized equilibrium emulsions always adjust to the slow changes in the system parameters. At first, the droplet size decreases due to hydrolysis-mediated formation of surface-active molecules on the time scale of a day. Surface tension of the bare oil−water interface is inversely related to the square of the emulsion droplet size. Subsequently, the emulsion droplets slowly grow again due to the gradual coating of the stabilizing particles by self-condensation of the hydrolyzed trialkoxysilane molecules on the surface. The coating of the colloids occurs more rapidly with larger fractions of TPM because of larger numbers of dissolved hydrolyzed TPM molecules, and leads to droplet growth in time, both in the absence and presence of excess oil. In both cases, the colloidal charge decreases, leading to closer approach of the colloids and less coverable interface in the absence of excess oil, and a decreased preferred curvature of the emulsion droplets in the presence of excess oil. Ultimately, the colloidal particles migrate into the oil phase and the emulsions phase separate into a colloid rich oil phase and an aqueous phase. While undergoing change in the chemical composition through formation of surface-active oil molecules and condensation thereof on the colloidal surface, the solid-stabilized emulsions always adapt their equilibrium size to the physical conditions created by the chemical process.

Here, we also note an analogy of this dynamic equilibrium with living polymers that spontaneously respond to changes in the amount of available monomer. We propose therefore to term this type of stable Pickering emulsions that respond to changes in the wetting properties of the stabilizing particles "living Pickering emulsions".

As a consequence, simply increasing the oil volume fraction does not achieve emulsion inversion into water-in-oil Pickering emulsions because the particles quickly transfer to the oil phase. So far, we have not succeeded in creating water-in-oil emulsions despite a variety of approaches. It would also be interesting to test for emulsification in the presence of colloidal particles that are originally dispersed in the oil phase. Such experiments could lead to a Pickering emulsion that does not undergo changes in the wetting properties of the colloidal particles and therefore stays uniform in time. This remains a challenge and motivation for future work on this system.

Supporting Information Available: Surface tension measurements for MPTES−TEM mixtures against water and 6 mM TMAH and additional photographs of sample flasks in time. This material is available free of charge via the Internet at http://pubs.acs.org.

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