

## Conditions for Equilibrium Solid-Stabilized Emulsions

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Particular types of solid-stabilized emulsions can be thermodynamically stable as evidenced by their spontaneous formation and monodisperse droplet size, which only depends on system parameters. Here, we investigate the generality of these equilibrium solid-stabilized emulsions with respect to the basic constituents: aqueous phase with ions, oil, and stabilizing particles. From systematic variations of these constituents, we identify general conditions for the spontaneous formation of monodisperse solid-stabilized emulsions droplets. We conclude that emulsion stability is achieved by a combination of solid particles as well as amphiphilic ions adsorbed at the droplet surface, and low interfacial tensions of the bare oil–water interface of order 10 mN/m or below. Furthermore, preferential wetting of the colloidal particles by the oil phase is necessary for thermodynamic stability. We demonstrate the sufficiency of these basic requirements by extending the observed thermodynamic stability to emulsions of different compositions. Our findings point to a new class of colloid-stabilized meso-emulsions with a potentially high impact on industrial emulsification processes due to the associated large energy savings.

### I. Introduction

Emulsions stabilized by solid particles, also called Pickering emulsions,<sup>1</sup> were for a long time believed to be thermodynamically unstable.<sup>2–4</sup> They do not form spontaneously but require energy input due to an increase in surface free energy upon droplet breakup. By adsorption of colloidal particles to the droplet surface, the energetically unfavorable oil–water interface is reduced and a mechanical barrier that retards the coalescence of the emulsions droplets is created. In the long term, oil and water phase separate again, and hence the emulsions are considered to be only of kinetic, but not of thermodynamic, stability.

A thermodynamically stable emulsion in contrast<sup>5,6</sup> forms spontaneously without any additional input of energy such as shaking or ultrasonication. The size of the emulsion droplets depends only on the components that determine the thermodynamic state of the system. Traditionally, only microemulsions, namely oil–water mixtures stabilized by surfactants and possibly cosurfactants, were considered to be thermodynamically stable. Only recently, a specific type of Pickering emulsion was discovered that exhibits thermodynamic stability. In the initial experiments, it was found that mixtures of a particular oil (3-(methacryloxypropyl)trimethoxysilane, TPM), water, and magnetite particles roughly 11 nm in size spontaneously formed oil-in-water emulsions with the solid particles adsorbed at the interface.<sup>5</sup> Later, spontaneous emulsification was also demonstrated for colloidal cobalt ferrite and Ludox silica.<sup>7</sup> Thermodynamic stability was deduced from mixing two emulsions with different droplet sizes that spontaneously evolved into a single emulsion with an intermediate droplet size. Furthermore, the monodisperse droplet size ranges between 30 and 150 nm and

is determined by the mass ratio of TPM and colloidal particles. Upon increase of the oil–colloid weight ratio, the droplet size grows linearly at first. Above a certain oil–colloid weight ratio, the droplet size reaches a constant value. Additional oil is expelled as a separate phase, in analogy to microemulsions.<sup>6</sup> Furthermore, the order of addition of the different components does not influence the outcome.

The late finding, historically speaking, of thermodynamically stable meso-emulsions poses the question whether the stability is due to a specific chemical composition, and therefore unique for a TPM oil phase and certain stabilizing colloids in aqueous media, or, whether it can be described in terms of more general physical parameters. In consideration of the wide range of possible applications and impact on energy efficiency of emulsification processes on industrial scales, a thorough understanding of the generality of the spontaneous emulsification is desirable.

Therefore, this article aims to elucidate the molecular origins of the thermodynamic stability of these Pickering emulsions, investigate the effect of the different components on the stability in detail, and compare experimental results with theoretical predictions. Specifically, we focus on the following issues:

- (1) emulsion stability in absence of colloidal particles;
- (2) ions present in the aqueous phase;
- (3) nature of colloidal particles that are adsorbed onto the oil–water interface; and
- (4) the nature of the oil.

We first review the current knowledge of the thermodynamically stable Pickering emulsions to motivate this choice of investigated parameters. Then, we describe the conducted experiments, discuss the results, and draw conclusions with respect to the basic requirements for thermodynamic stability.

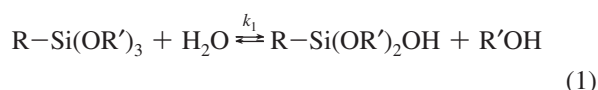
### II. Review of Previous Work

Emulsification of a macroscopic oil and water phase into small droplets significantly enlarges the interfacial area between

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the oil and water phase. Adsorption of colloidal particles onto the droplet surface partially decreases this interfacial area, reducing the energy necessary to create such an interface. Yet, at least 10% of the interfacial area remains uncovered. The energy required to create that bare interface depends on the interfacial tension between oil and water phase. Previously, it was measured that the bare oil–water interfacial tension is as low as 3 mN/m,<sup>8</sup> much higher than the ultralow interfacial tensions of microemulsions, but still low compared to common oil–water interfacial tensions, being typically 50 mN/m. The low interfacial tension between TPM–oil and water phase is achieved by partial hydrolysis of the alkoxy moieties of TPM, a process catalyzed in alkaline environment. Alkalinity is a result of the complete dissociation of the quaternary ammonium salt tetramethylammonium hydroxide (TMAH) present in the aqueous colloidal suspension. Trialkoxysilanes such as TPM undergo hydrolysis in dilute aqueous solutions via a series of consecutive reactions, of which the first one is



where, in the case of TPM,  $\text{R} = \text{H}_2\text{CC}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3$  and  $\text{R}' = \text{CH}_3$ . Consecutive hydrolysis steps take place at a slower rate than the first.<sup>9</sup> The reaction product methanol in TPM hydrolysis in the presence of TMAH was detected by NMR measurements.<sup>8</sup>

After formation, the weakly acidic silanol groups can dissociate according to



creating negatively charged molecules that are surface active due to their amphiphilic nature. The adsorption to the interface was verified by observing a decrease in the interfacial tension between TPM and aqueous 6 mM TMAH from 8 mN/m down to 3 mN/m over the course of 24 h. Furthermore, self-condensation between the modified TPM molecules might play an undesired role in the stability. However, condensation of hydrolyzed TPM is a much slower process than the initial hydrolysis. Addition of NaCl salt to an equilibrated emulsion in the presence of an excess oil phase increased the droplet size significantly, hinting at a charge induced preferred curvature of the droplets.<sup>5</sup>

Due to these very specific requirements, it is as of yet unclear whether the thermodynamic stability of solid-stabilized emulsions can be extended to other oils and colloidal particles. Recently, theoretical progress has been made on describing the underlying physics in two distinct regimes of emulsion stability.<sup>10,11</sup> The models are complementing each other as they are applicable to the one-phase and the two-phase region, that is, in the absence and presence of excess oil, respectively.

In the linear growth regime and absence of excess oil, Zwanikken et al. concluded that spontaneous emulsification is possible for hydrophobic, charge-stabilized colloidal particles, amphiphilic salt ions, and hydrolyzable oil.<sup>11</sup> The adsorption of charged colloidal particles to the oil–water interface can compensate the surface charge of the bare oil–water interface created by dissociated, hydrolyzed TPM molecules. Positive ions ( $\text{TMA}^+$ ) are assumed to preferentially adsorb onto the colloidal particles, whereas the reactivity of the oil creates negatively charged molecules adsorbed at the oil–water interface. As long

as the net surface charge of the droplet remains low, the surface tension can decrease even to negative values. A finite droplet radius and thermodynamic stability of the solid-stabilized droplets is found at an optimal value for the ratio of colloid surface in contact with water over free oil interface.<sup>11</sup>

For the two-phase regime, Kegel et al. proposed that adsorption of hydrophobic colloids that preferably are wetted by the oil phase to the oil–water interface releases ions from the chargeable groups of the colloidal surface.<sup>10</sup> Compared to the immersion in the oil phase, the ion dissociation yields an entropic contribution to the free energy of the droplets which can balance the unfavorable free energy necessary for creating bare oil–water interface. At surface tensions of the bare oil–water interface on the order of 1 mN/m, a global minimum in the free energy was found for a finite droplet size. The subtle balance in the interfacial tensions between colloids and oil,  $\gamma_{\text{co}}$ , colloids and water,  $\gamma_{\text{cw}}$ , and oil and water,  $\gamma_{\text{ow}}$ , determines droplet stability. Thermodynamic stability is achieved for  $-0.4 \leq (\gamma_{\text{co}} - \gamma_{\text{cw}})/\gamma_{\text{ow}} \leq -0.2$ . Furthermore, an upper limit for the particle size that yields emulsion stability was predicted.

Both models take negatively charged colloidal particles that have a preference for the oil phase, and low interfacial tensions between the bare oil–water interface, into account.

This incomplete picture of spontaneous emulsification into solid-stabilized oil droplets motivated us to systematically investigate the different constituents.

First, we examine whether thermodynamic stability of the emulsions can be obtained in the absence of the colloidal particles by mixing TPM and water containing TMAH salt.

To examine the influence of TMAH, and salts in general, on the stability, we use dialyzed colloidal silica with different types of salts added in a controlled manner.

Subsequently, we explore emulsion stability with respect to different colloidal particles, ranging from nanometer-sized gold colloids to silica colloids of up to roughly 200 nm in diameter. Here, size, charge, and material of the colloids are considered when drawing conclusions on thermodynamic stability.

Finally, the specificity of the molecular structure of the oil phase that is required to obtain thermodynamically stable emulsion droplets is studied by systematically varying the different moieties of the trialkoxysilane oil as well as by employing linear alkanes and cycloalkanes. Conclusions on the conditions of thermodynamic stability are employed to find emulsions composed of a different oil phase, counterions, and colloidal particles that still exhibit thermodynamic stability. Given the various experiments that corroborated thermodynamic stability in these Pickering emulsions,<sup>5,7,8</sup> we limit ourselves to testing the emulsions for stable monodisperse droplet sizes.

### III. Experimental Section

**A. Colloidal Dispersions.** Water used for syntheses and experiments was of Millipore purity.

Colloidal magnetite dispersions ( $\text{Fe}_3\text{O}_4$ ) were prepared following a precipitation method described by Massart.<sup>12</sup> Forty milliliters of a 1 M aqueous solution of  $\text{FeCl}_3$  and 10 mL of an acidic (2 M HCl) aqueous solution of 2 M  $\text{FeCl}_2$  were combined and quickly added to 500 mL of 0.7 M  $\text{NH}_4\text{OH}$  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 a quaternary ammonium salt. To vary the type of ions present in the colloidal dispersion, magnetite dispersions were prepared with either a tetramethylammonium hydroxide (TMAH) or a tetraethylammonium hydroxide (TEAH) solution. The magnetite particles were

subsequently transferred to Millipore water via magnetic decantation. The final dispersion contained nonaggregated, negatively charged magnetite colloids with an average diameter of  $11\text{ nm} \pm 28\%$  (TMAH stabilized) and  $12\text{ nm} \pm 30\%$  (TEAH stabilized). Aqueous magnetite is known to oxidize to maghemite in time. Even though no influence on emulsion stability could be detected and therefore no measures were taken to control the oxidation state, it may be useful to use a standard oxidation state in future experiments.<sup>13</sup>

Similarly, aqueous dispersions of cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoparticles of  $20\text{ nm} \pm 27\%$  were prepared by the coprecipitation of iron chloride and cobalt chloride salts, as described by Claesson et al.,<sup>13</sup> based on the procedure developed by Tourinho et al.<sup>14</sup> First,  $2.38\text{ g}$  ( $0.01\text{ mol}$ ) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was dissolved in a solution of  $1\text{ mL}$  of  $\text{HCl}$  (37%) and  $4\text{ mL}$  of water, and  $5.406\text{ g}$  ( $0.02\text{ mol}$ ) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in  $40\text{ mL}$  of water. These solutions were both heated to  $50\text{ }^\circ\text{C}$ , and subsequently mixed and quickly added to a  $200\text{ mL}$  solution of boiling  $1.0\text{ M}$  aqueous  $\text{NaOH}$  under vigorous stirring. After stirring for  $30\text{ min}$  at  $100\text{ }^\circ\text{C}$ , 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  $100\text{ mL}$  of  $\text{H}_2\text{O}$ . This procedure was used to rinse the particles 4 times with  $100\text{ mL}$  of  $\text{H}_2\text{O}$ . The resulting sediment was redispersed in  $30\text{ mL}$  of  $2.0\text{ M}$   $\text{HNO}_3$  and stirred for  $5\text{ min}$ , upon which  $30\text{ mL}$  of  $0.35\text{ M}$   $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added. The reaction mixture was refluxed for  $45\text{ min}$ , 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  $50\text{ mL}$  of  $1\text{ M}$  TMAH overnight under stirring. Finally, the particles were sedimented on a magnet to remove the excess of TMAH and redispersed in approximately  $60\text{ mL}$  of  $\text{H}_2\text{O}$ .

Ludox AS-40 silica dispersions (DuPont) containing  $50\%$  w/w amorphous colloidal silica with a diameter of  $25\text{ nm} \pm 18\%$  in an aqueous ammonium hydroxide solution were diluted with Millipore water to  $10.36\%$  w/w. A  $100\text{ mL}$  volume of this silica dispersion was dialyzed against demi water for 5 days during which the water was changed four times. After filtration through  $0.2\text{ }\mu\text{m}$  Millipore filters and further dilution, an aqueous dispersion of  $2.85\%$  w/w nonaggregated silica was obtained.

Bindzil 30/360 colloidal silica dispersion containing particles  $5\text{--}8\text{ nm}$  in diameter at  $30\%$  w/w was obtained from EKA, Akzo Nobel. The Bindzil dispersion was diluted to  $2.33\%$  w/w for emulsion experiments.

Furthermore, a silica dispersion containing particles with a diameter of  $203\text{ nm} \pm 4.7\%$  was synthesized in ethanol according to the Stöber method.<sup>15</sup> After transfer to Millipore water, the dispersion was prepared at volume fractions of  $1.0\%$  w/w.

Polystyrene particles of  $113\text{ nm}$  ( $7\%$  w/w,  $3\%$  w/w divinylbenzene) were prepared by emulsion polymerization in aqueous solution as described previously.<sup>16,17</sup> A fraction of the polystyrene particles was subsequently coated with vinyl acetate to render them more hydrophilic.<sup>17</sup>

A colloidal dispersion containing gold colloids of about  $20\text{ nm}$  in diameter was made via the Turkevich–Frens method.<sup>18,19</sup> For this,  $250\text{ mL}$  of a  $0.01\%$  w/w  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Sigma Aldrich, used as received) aqueous solution was brought to the boil under vigorous stirring. When boiling,  $3.8\text{ mL}$  of a  $1\%$  w/w sodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ , Merck) aqueous solution was added and boiling was continued for approximately  $5\text{ min}$  during which the solution turned dark purple. The final

suspension contained  $0.09\%$  w/w colloidal gold ( $20\text{ nm}$  diameter). The dispersion was dialyzed against demi water, and the pH of the colloidal dispersion was raised to 7 with TMAH.

Furthermore, a dispersion of colloidal gold capped with 4-mercaptobenzoic acid (4-MBA) was prepared following a modified method of Buining,<sup>20</sup> Reincke,<sup>21</sup> and Brust.<sup>22</sup> For this,  $10.0\text{ mL}$  of Millipore water was mixed with  $200\text{ }\mu\text{L}$  of aqueous  $\text{HAuCl}_4$  solution ( $4.61\text{ mg/mL}$ ) and  $200\text{ }\mu\text{L}$  of 4-MBA in ethanol ( $0.233\text{ mg/mL}$ ). Under vigorous stirring, the hydrogen tetrachloroaurate was reduced by addition of  $200\text{ }\mu\text{L}$  of a  $100\text{ mM}$  aqueous sodium borohydride solution ( $\text{NaBH}_4$ ). The pH was adjusted by addition of aqueous TMAH to pH 9. The final suspension contained  $1.4\%$  w/w colloidal gold with a diameter of  $3.5 \pm 1.5\text{ nm}$ .

## B. Emulsion Preparation.

**General Procedure for Emulsion Preparation.** Unless stated otherwise, the components were added in no specific order as the final state of a thermodynamically stable system is only depending on the relative amounts of the components and not on the sequence of addition.<sup>5</sup> After preparation, the samples were stored on a vibration-free table in a dark, temperature-controlled room. Especially when oils containing an acrylic group, such as 3-(methacryloxypropyl)trimethoxysilane (TPM, Acros Organics, used as received), was used as the oil phase, exclusion of light as well as elevated temperatures are important in order to avoid spontaneous polymerization upon exposure to UV light or heat.

**Polymerization.** Polymerization of the particle stabilized TPM droplets was done either by addition of potassium persulfate ( $0.5\text{ mL}$  of  $23\text{ mg/mL}$  aqueous KPS per  $3\text{ mL}$  of emulsion) at  $70\text{ }^\circ\text{C}$  or by exposure to UV light ( $180\text{ W}$ ,  $\lambda = 365\text{ nm}$ , Fluolink Flex, New Brunswick;  $100\text{ min}$  exposure, samples placed in optical glass cuvettes with  $10\text{ mm}$  thickness) in the presence of  $2\%$  w/w Irgacure ((2,4,6-trimethylbenzoyl, Ciba) in the TPM phase at room temperature. Furthermore, acidic as well as strong alkaline conditions above pH 10 are to be avoided because they lead to rapid self-condensation reactions of the oil and, in the case of solid silica particles, significant dissolution of colloidal silica for pH > 9. All samples were polymerized by radical initiation through KPS unless mentioned otherwise.

## Mixtures of TPM and TMAH in the Absence of Colloids.

The necessity of colloidal particles for the emulsion formation was investigated by addition of different aliquots of TPM oil ( $50, 100, 150, 200$ , and  $250\text{ }\mu\text{L}$ ) to  $10.0\text{ mL}$  of a  $6\text{ mM}$  TMAH in Millipore water solution. The concentration of TMAH corresponds to pH 9 as measured.

**Different Colloidal Particles.** Emulsions containing TPM and colloidal particles of different sizes and materials at colloid concentrations mentioned above were prepared to investigate the influence of size and material of the colloidal particles.

**Nature of Salt.** To investigate the effect of the nature of ions present in the system, we prepared several series containing dialyzed Ludox silica colloids ( $12.0\text{ g}$  of  $1\%$  w/w colloidal silica per sample) as well as  $1\text{ mL}$  of Millipore water,  $1\text{ mL}$  of  $0.1\text{ M}$   $\text{NaOH}$ ,  $1\text{ mL}$  of  $0.1\text{ M}$  TMAH,  $1\text{ mL}$  of  $0.1\text{ M}$  TEAH, or  $1\text{ mL}$  of  $0.1\text{ M}$  tetrapropylammonium hydroxide (TPAH). These salts were chosen in order to test whether hydroxide molecules that hydrolyze TPM, and thereby induce low interfacial tensions, are sufficient for emulsion stability. The concentrations of ions were chosen such that the pH in the final solution was 9–10. For each series we prepared four samples with increasing concentrations of TPM, such that the weight ratios  $m_{\text{TPM}}/m_{\text{colloid}}$  were 0.9, 1.5, 2.2, and 2.9.



**Nature of Oil.** 3-(Methacryloxypropyl)trimethoxysilane (TPM) was used as received from Acros Organics in different concentrations as described in the respective experiments. Besides TPM, other oils were used to explore the influence of different chemical moieties on the thermodynamic stability of the emulsions. In TPM, the methacrylate allows for polymerization of the oil by radical initiators or UV light. The methoxy groups can be hydrolyzed in the presence of hydroxide to render the silane group negatively charged, thereby creating an amphiphilic molecule. All oils used in mixtures with TPM were tested for macroscopic mixing with TPM to exclude possible phase separation of the two oils.

**Dodecane/Octane/Cyclohexane.** TMAH-magnetite stabilized emulsions were prepared with dodecane (99%, used as received from Acros Organics), octane (99%, used as received from Acros Organics), and cyclohexane (p.a., used as received from Mallinckrodt Baker) as the respective oil phases at an oil–colloid weight ratio  $m_{\text{TPM}}/m_{\text{colloid}} = 7$ . These experiments were conducted to determine whether alkane and cycloalkanes can form thermodynamically stable emulsions. DLS measurements were performed 1 day after preparation. Then, 10% w/w TPM with respect to the total oil mass was added to the emulsions. DLS measurements were performed again after 1 and 6 days of equilibration.

**(3-Methacryloxypropyl)triethoxysilane (MPTES).** We further used MPTES 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 (see also Table S1, Supporting Information). The ethoxy groups of the oil are more resistant to hydrolysis while MPTES is still having a chemical structure similar to TPM. From these experiments, the influence of the hydrolyzation product on thermodynamic stability can be determined.

**(3-Mercaptopropyl)trimethoxysilane.** In addition, emulsions were prepared from (3-mercaptopropyl)trimethoxysilane (Sigma Aldrich, used as received) and 10.00 g of 0.125% w/w TMAH stabilized magnetite dispersion to obtain an oil–colloid weight ratio  $m_{\text{oil}}/m_{\text{colloid}} = 6.4$ . (3-Mercaptopropyl)trimethoxysilane has chargeable trimethoxysilane and apolar propyl group in common with TPM, but contains a mercapto instead of the methacryloxy group (see also Supporting Information). Here, the influence of the molecular specificity of the apolar tail group was investigated.

**(3-Mercaptopropyl)triethoxysilane.** Similarly, emulsions were also prepared from (3-mercaptopropyl)triethoxysilane (tech., >80%, Sigma Aldrich, used as received) and 10.00 g of 0.125% w/w TMAH stabilized magnetite dispersion to obtain an oil–colloid weight ratio  $m_{\text{oil}}/m_{\text{colloid}} = 6.4$ . (3-mercaptopropyl)triethoxysilane is an oil with a chemical structure similar to that of (3-mercaptopropyl)trimethoxysilane with only the methoxy groups exchanged for ethoxy groups. Combined with the experiment on (3-mercaptopropyl)trimethoxysilane, use of this oil should elucidate any correlation between emulsion stability and the mercapto group, as well as the necessity of the methoxy/ethoxy group for thermodynamic stability, respectively.

Please refer to the Supporting Information for tables with the chemical formulas of the different oils (Table S1) and salts (Table S2) used in this article.

**C. Characterization. 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.

**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.

**Zeta Potential.** Zeta potentials were measured on diluted emulsions with a Malvern Zetasizer Nano at 25 °C.

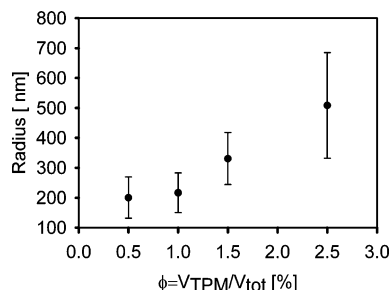
**Interfacial Tension.** The surface tensions of various oils embedded in a 6 mM aqueous TMAH phase were determined at 25 °C using a spinning-drop tensiometer. The samples were prepared by first filling glass tubes with the denser phase, after which droplets of the lighter phase were injected. For mixtures of TPM/MPTES, 10/90 50% D<sub>2</sub>O was used in the aqueous phase to obtain a density of 1.05 g/cm<sup>3</sup>. 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 in the centrifugal field as a function of the rotational speed, using the Vonnegut equation:  $\gamma = (\Delta\rho\omega^2r^3)/4$ , which is valid if  $l > 8r$ . 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. The change in density of the aqueous phase upon addition of ions was taken into account.

## IV. Results and Discussion

### 1. Emulsion Stability in the Absence of Colloidal Particles.

Solid-stabilized emulsions consist of four constituents: an aqueous phase containing dissolved salts, an oil phase and solid colloidal particles. To test for the necessity of colloidal particles in the stabilization of the emulsion droplets, we first investigated the behavior of mixtures of TPM and aqueous TMAH without colloidal particles. The presence of TMAH furthers hydrolysis of TPM not only by shifting the pH toward alkaline conditions but it probably acts as a catalyst in the reaction. In kinetic studies of the hydrolysis of TPM triethylamine, similar in chemical structure to the positive tetramethyl ammonium ion, was found to catalyze the hydrolysis, but also to speed up the self-condensation reaction of the formed silanols into siloxane linkages.<sup>23</sup> Hydrolyzed TPM molecules can dissociate forming negatively charged silane groups that consecutively lower the interfacial tension between the oil and the water phase. Samples containing different volume fractions of TPM (between 0.5 and 2.5% v/v) at a fixed concentration of TMAH (6 mM), but without colloidal particles, turned turbid within a day after gentle mixing. The turbidity increased with the TPM volume. After several days, the emulsions became unstable and phase separation occurred. TEM measurements on TPM droplets polymerized one day after preparation show large, highly polydisperse TPM droplets (see Supporting Information, Figure S1).

Despite the system being a thermodynamically unstable emulsion, at a given point in time before phase separation, the average droplet size increases linearly with the volume fraction of TPM,  $\phi$ , as shown in Figure 1. We can even conclude that the average droplet size increases linearly with the ratio of the concentration of TPM to TMAH in the absence of stabilizing solid particles. Since the concentration of TMAH was equal in all experiments, the concentration of the hydroxide ions,  $[\text{OH}^-]$ , and hence the concentration of hydrolyzed TPM is in first approximation constant throughout the series. Then, the oil–water interfacial area  $A_{\text{oil}}$  that can be occupied by surface-active TPM molecules obtained from hydrolysis is constant as well, and the radius of the droplets should scale linearly with the volume of the TPM phase, since  $R = 3V_{\text{oil}}/A_{\text{oil}}$ . Indeed, this can be seen in



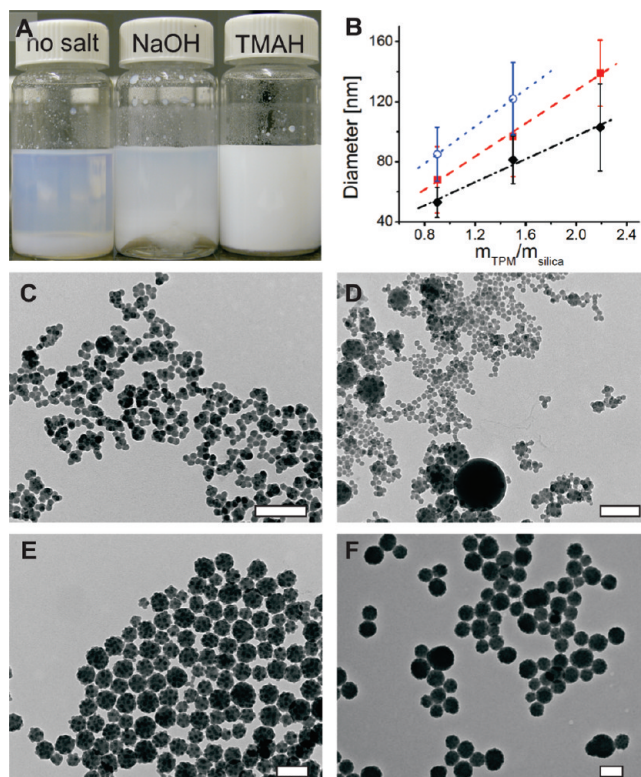
**Figure 1.** Even though mixtures of TPM in 6 mM aqueous TMAH solution are not stable, emulsion droplets show an approximately linear increase with the TPM concentration 1 day after mixing.

Figure 1. Why the system chooses this unusual path of emulsification and phase separation is unclear. A possible mechanism could be self-emulsification induced, for example, by local supersaturation or preferential diffusion of hydrolyzed TPM molecules into the water phase. Emulsions formed by self-emulsification are generally metastable.<sup>24</sup> In contrast, in the presence of colloidal particles, significantly smaller monodisperse and stable droplets were found. Thermodynamic stability was demonstrated by spontaneous formation of intermediate droplet sizes from two emulsions with different average droplet sizes.<sup>5</sup> We therefore conclude that for the formation of equilibrium solid-stabilized emulsions self-emulsification may play a role in the initial emulsification, but is not the reason for its thermodynamic stability. For stability, another component than just hydrolyzing ions, and an oil and aqueous phase, is required.

**2. Ions Present in the Aqueous Phase.** Tetramethylammonium ions have been hypothesized to play a role in emulsion stabilization,<sup>8</sup> not only by raising the pH and catalyzing hydrolysis of TPM but possibly also by adsorbing onto the colloidal particles and the oil–water interface.<sup>11</sup>

To investigate the significance of salts on thermodynamic stability, we dialyzed Ludox silica colloids and prepared emulsions with these colloids containing no salt, 7.7 mM NaOH, TMAH, TEAH, or TPAH, respectively. The samples with salts had pH 9, whereas the sample without salt was at neutral pH. This pH value was chosen because it induces hydrolysis of TPM on the time scale of 24 h without leading to rapid self-condensation reactions of the oil and, in the case of solid silica particles, significant dissolution of colloidal silica. In the presence of the quaternary ammonium salts (TMAH, TEAH, and TPAH), the mixtures quickly turned turbid, indicating emulsification. The sample containing sodium hydroxide only slightly increased turbidity of the liquid phase and had a clear phase consisting of TPM at the bottom of the flask. In the absence of any of those salts, and therefore at a neutral pH, no emulsification occurred, which is clearly visible by the transparent white aqueous phase and the white TPM phase at the bottom. Photographs of the samples that illustrate the effect of the presence and type of salt during emulsification are shown in Figure 2A.

After polymerization of a fraction of the top phase, we imaged all samples with a transmission electron microscope (TEM). In the absence of salt, we find many free silica particles as well as small clusters (Figure 2C). With sodium hydroxide in the aqueous phase the silica colloids are free, clustered, or attached to small droplets (Figure 2D). In the presence of quaternary ammonium salts (TMAH, TEAH, and TPAH), we have never observed free silica particles in solution. All colloids are adsorbed onto emulsion droplets (Figure 2E,F, and Supporting Information, Figures S2 and S3). Even though the pH in all



**Figure 2.** (A) Mixtures of dialyzed Ludox AS 40 silica colloids, TPM, and water, NaOH, or TMAH. Without ions, a white sediment is observed, whereas for NaOH most of the oil remains on the bottom of the flask. In the presence of TMAH, emulsification occurs, indicated by an increase in turbidity. (B) Linear dependence of the droplet diameter on the oil TPM–silica ratio as a function of added quaternary ammonium salt: 7 mM (○) TMAH, (■) TEAH, and (◆) TPAH. With increasing length of the alkyl group, the droplet size increases at a given oil–colloid weight ratio. Emulsions of 2.85% w/w dialyzed Ludox silica dispersions and TPM were prepared using (C) no salt, (D) 7.7 mM NaOH, (E) 7.7 mM TMAH, or (F) 7.7 mM TEAH. Emulsions are formed in the presence of the quaternary ammonium salts (E, F), but not without salt or with NaOH (C, D). Transmission electron micrographs shown are for a TPM–silica mass ratio 2.2. Scale bars are 200 nm.

samples containing salts were equal, only the ones containing quaternary ammonium salts emulsified significantly. The hydroxide molecules present are hydrolyzing TPM into surface-active molecules as described by the net reaction 1. However, this experiment shows clearly that hydroxide molecules alone are insufficient for stabilization. Surface tension measurements between TPM and water containing either NaOH or TMAH showed no significant difference 24 h after preparation (Table 1). Both lie around 10 mN/m. Even if TMAH acts as a catalyst in the hydrolysis of TPM, it does not lead to a difference in the interfacial tension on the time scale of emulsion formation. Similarly, mixtures of Bindzil colloids with 7.7 mM NaOH and 7.7 mM TMAH were prepared and monodisperse emulsion droplets that formed spontaneously were observed only in the presence of TMAH (see Figure 3G,H and Supporting Information, Figure S5).

Due to their amphiphilic nature, the positively charged tetramethylammonium ions are more likely to adsorb on the interface. As a result, they reduce both the negative colloidal as well as interfacial charge from surface-active TPM molecules more efficiently than ions in solution alone. This behavior is not expected for sodium ions and could therefore explain the difference in stability.

**TABLE 1: Emulsion Stability for Different Types of Colloidal Particles**

colloidal material	colloidal diameter (nm)	emulsion stable in the presence of TMAH?
4-MBA-capped gold	3.5 ( $\pm 43\%$ )	yes
citrate-capped gold	20	no
magnetite stabilized by TMAH	11 ( $\pm 28\%$ )	yes
magnetite stabilized by TEAH	12 ( $\pm 30\%$ )	yes (no extra TMAH used)
cobalt ferrite stabilized by TMAH	20 ( $\pm 27\%$ )	yes
Bindzil silica 30/360	5–8	yes
Ludox silica AS	25 ( $\pm 18\%$ )	yes
Stöber silica	203 ( $\pm 4.7\%$ )	no
sulfated polystyrene	226 ( $\pm 2.5\%$ )	no
vinyl acetate coated polystyrene	222 ( $\pm 2.5\%$ )	no

Another interesting observation is that the silica-covered TPM droplets stabilized by quaternary ammonium salts change size depending on the oil–colloid weight ratio  $m_{\text{oil}}/m_{\text{colloid}}$  (Figure 2B) in the single-phase region. The linear size increase with the oil–colloid weight ratio is in contrast to previous observations on Ludox silica colloids in an aqueous ammonium hydroxide solution used as received.<sup>7</sup> There, emulsification occurred spontaneously above a threshold ratio  $m_{\text{oil}}/m_{\text{colloid}} = 1.3$ , and the droplet size remained constant upon further increase of the oil concentration. Below an oil–colloid weight ratio of 1.3, electron micrographs showed uncovered TPM droplets and free silica colloids. Using silica colloids with salt added after dialysis, we also found spontaneous emulsification at a ratio  $m_{\text{oil}}/m_{\text{colloid}} = 0.9$  (Supporting Information, Figures S2, S3, and S4). The linear size increase with the oil–colloid weight ratio is analogous to previous results obtained for TPM droplets stabilized by colloidal magnetite in the presence of TMAH in the single-phase region.

Furthermore, note that, at a given oil–colloid weight ratio, the droplet size increases with the length of the alkyl group of the ions. A longer alkyl group implies stronger amphiphilicity of the ion, which apparently is more efficient in reducing the negative charge of the colloidal particles and surface-active TPM molecules upon adsorption at the interface. The better the charge between the colloidal particles is screened, the smaller the surface area they occupy is and the larger the droplet size at equal oil volumes must be. However, the net surface charge of the emulsion droplets remains low. For a magnetite stabilized TPM emulsion (oil–colloid mass ratio of 10, diameter  $152 \pm 3$  nm) the zeta potential was measured to be  $-1.5 k_B T/e$ . That equals to roughly 350 negative elementary charges for an ionic strength of 7 mM. For further images and experimental details on experiments with dialyzed Ludox and Bindzil silica particles, see Supporting Information, sections 2 and 3.

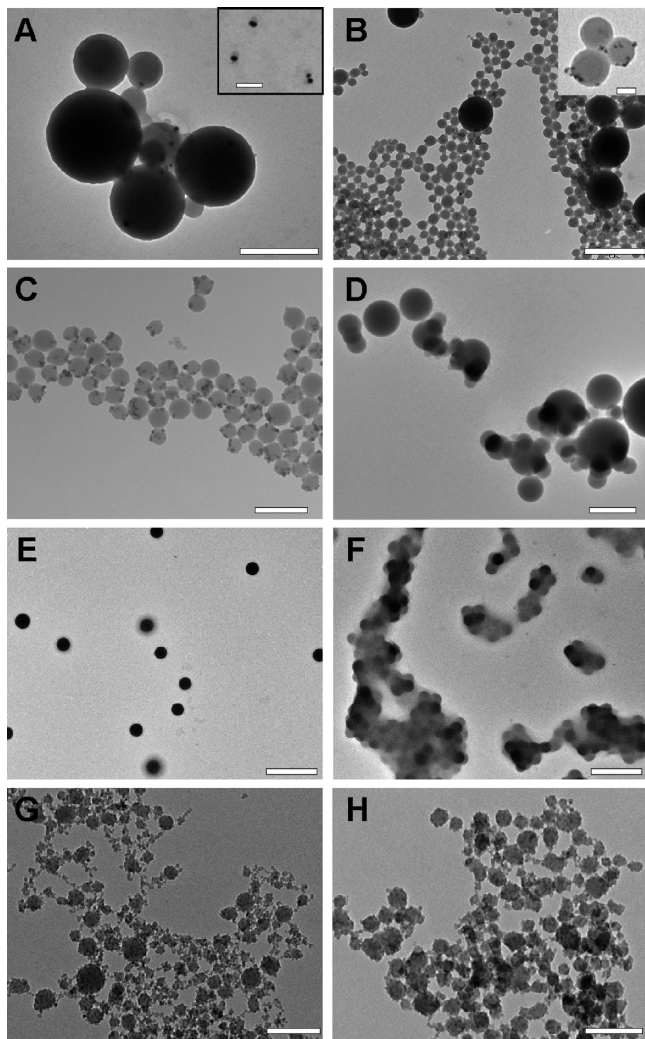
Such direct comparisons of droplet sizes obtained from different batches of magnetite or cobalt ferrite stabilized by TMAH and TEAH cannot be made due to the insufficient control over ion removal during magnetic decantation: different batches can contain different concentrations of quaternary ammonium salts. Zeta potential measurements give information on the charge of the colloidal particles and therefore indirectly on the concentration of stabilizing salt. For magnetite (TMAH and TEAH stabilized) and cobalt ferrite (TMAH stabilized) colloids the zeta potential was measured to be  $-1.6 \pm 0.3 k_B T/e$ ,  $-2.0 \pm 0.3 k_B T/e$ , and  $-2.2 \pm 0.4 k_B T/e$ , respectively. Qualitatively, the increase in droplet size as a function of the oil–colloid mass ratio is always the same, as depicted in Figure S7, Supporting Information. However, the slope of the increase in the droplet size with the oil volume and the droplet size in the presence of an excess oil phase may vary. In the one-phase region the slope of the droplet size increase as a function of the

oil–colloid mass ratio is larger for TMAH than for TEAH stabilized magnetite colloids.

**3. Type of Stabilizing Colloidal Particles.** To achieve thermodynamically stable Pickering emulsions, different types of colloidal particles were used in TPM–water systems: TMAH stabilized magnetite and cobalt ferrite, and commercial Ludox AS 40 silica.<sup>7</sup> However, it is still unknown how broad a range in material, size, and properties of the colloidal particles can be used to stabilize these emulsions. This is both interesting with respect to possible applications as well as for the understanding of the mechanism of emulsification. We used different colloidal particles with a variety of materials, sizes, and stabilizing ions in emulsion experiments with TPM as the oil phase: 11 nm TMAH- and 12 nm TEAH-stabilized magnetite, TMAH-stabilized cobalt ferrite of 20 nm, Ludox AS 40 silica of 25 nm, Bindzil 30/360 silica colloids of 5–8 nm, Stöber silica of 203 and 310 nm, polystyrene of 226 nm, both pure polystyrene as well as with a hydrophilic coating of vinyl acetate, and gold colloids 20 nm in diameter with citrate capping as well as gold colloids of 3.5 nm with 4-mercaptopbenzoic acid (4-MBA) capping. Without any additions to the colloidal suspensions as obtained from synthesis mixtures containing magnetite, cobalt ferrite and Ludox silica colloids were found to form monodisperse, stable emulsions. However, droplet stability could not be obtained by Bindzil silica, Stöber silica, polystyrene, or gold colloids in aqueous solution. Whereas the 25 nm Ludox silica particles formed stable emulsions, the smaller Bindzil and the larger Stöber silica particles were incapable of achieving this despite the similarity in material. Emulsification failure might be due to the absence of TPM hydrolyzing molecules that lower the oil–water interfacial tension by creating surface-active molecules. As previously shown for dialyzed Ludox silica, colloidal particles suspensions alone that do not contain hydrolyzing agents such as TMAH (magnetite and cobalt ferrite) or ammonia (Ludox silica) are not sufficient for droplet stability.

Therefore, we prepared emulsions of TPM and colloidal particles in aqueous 6 mM TMAH solution that previously did not spontaneously emulsify. In the case of uncapped gold colloids, polydisperse droplets are seen on TEM images of polymerized emulsions. Small droplets contain only one or a few gold colloids, whereas the larger droplets do often not have any gold particles attached (Figure 3A). 4-MBA-capped gold colloids exhibit bidisperse TPM emulsion droplets sparsely covered with colloidal particles (see Figure 3B). The inset shows that the smaller droplet species resembles typical stable Pickering emulsions. The large uncovered droplets may be due to an excess of TPM. This improvement in stabilizing capability compared to the citrate-capped gold colloids could be due to the more hydrophobic 4-MBA-coated surface.<sup>25</sup> No emulsification was obtained with Stöber silica and polystyrene particles.





**Figure 3.** Polymerized samples of mixtures of TPM with different stabilizing colloidal particles. (A) Polydisperse emulsion droplets with each only one adsorbed citrate capped gold colloid (scale is 500 nm). Inset shows small droplets that were frequently observed (scale is 100 nm). (B) Bidisperse droplets are visible after polymerization when 4-MBA-coated gold colloids are mixed with TMAH and TPM (scale is 500 nm). Inset shows a blowup of the smaller species with gold colloids adsorbed to the interface (scale is 40 nm). (C) TEAH-stabilized magnetite readily emulsifies TPM into monodisperse emulsion droplets (scale is 200 nm). (D) Stöber silica colloids adsorb at the interface of TPM droplets, but do not form monodisperse emulsion droplets (scale is 500 nm). (E) Sulfated polystyrene colloids in 6 mM TMAH and mixed with TPM lead to growth of the individual particles, but not to emulsion droplets (scale is 1  $\mu$ m). (F) Vinyl-acetate-coated sulfated polystyrene colloids in 6 mM TMAH and mixed with TPM are aggregating, but do not show monodisperse droplet sizes (scale is 1  $\mu$ m). (G) Similarly to Ludox silica as shown in Figure 2, mixtures of Bindzil silica colloids in 7.7 mM NaOH and TPM contained polydisperse droplets as well as free silica colloids (scale is 200 nm). (H) In the presence of 7.7 mM TMAH, Bindzil silica colloids and TPM form stable emulsion droplets (scale is 200 nm).

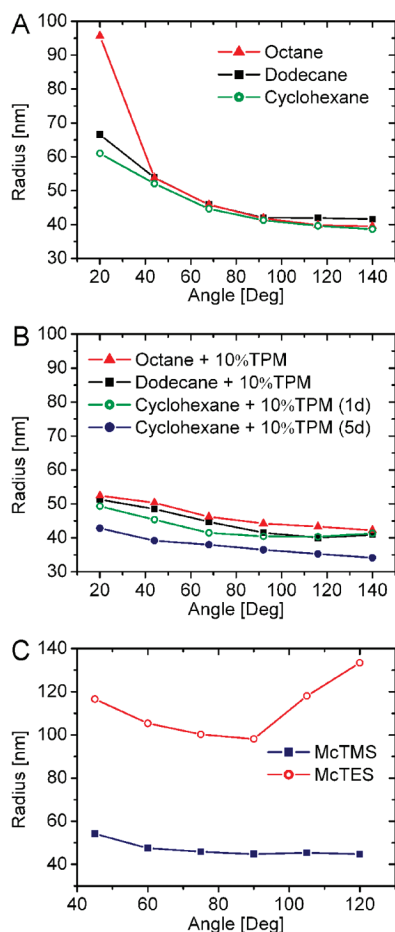
TEM pictures of polymerized samples show polydisperse TPM droplets and free silica particles, with only a few colloids adsorbed to emulsion droplets (Figure 3D). For sulfated and vinyl-acetate-coated polystyrene particles, emulsification was not obtained either (Figure 3E,F). On the other hand, emulsions containing TEAH-stabilized magnetite colloids readily emulsified as supported by TEM images of polymerized samples (Figure 3C). Dialyzed Bindzil colloidal particles readily form emulsions in the presence of 7.7 mM TMAH (Figure 3H), whereas polydisperse droplets and free silica particles are

observed in the presence of NaOH (Figure 3G, and Supporting Information Figure S5 and S6). Hematite spindles stabilized with TMAH and with a long axis of 250 nm were also found to spontaneously induce emulsification, but did not exhibit thermodynamic stability.<sup>8</sup>

It was theoretically predicted that a condition for thermodynamically stable emulsions is that colloidal particles though initially dispersed in the aqueous phase are preferentially wetted by the oil phase.<sup>10,11</sup> Preferential wetting of magnetite particles by the oil phase was also found previously in wetting experiments with water and TPM on a macroscopic polished magnetite surface.<sup>5</sup> Besides, colloidal particles that do achieve emulsification, such as magnetite, cobalt ferrite, silica, and 4-MBA-capped gold, are more hydrophobic than the ones that failed emulsification, such as citrate-capped gold, sulfated, and vinyl-acetate-coated polystyrene. Furthermore, we have observed that colloidal particles with which stable emulsions are achieved transfer into the oil phase on the time scale of days to weeks.<sup>25</sup> This is possibly caused by a slow chemical process such as self-condensation of TPM on the particle surface and happens on a different time scale.<sup>25</sup> Moreover, formation of stable monodisperse emulsions was found only for negatively charged particles that do not exceed 203 nm in diameter. Zeta potentials for magnetite and cobalt ferrite were around  $-2 k_B T/e$ , as mentioned earlier.

**4. Nature of the Oil.** TPM plays an important role in the spontaneous emulsification because the molecules exposed to the aqueous TMAH phase are hydrolyzed and consecutively charged by dissociation. Next, we investigate whether the thermodynamic stability is specific to the chemical structure of TPM or if a common physical property can be identified. In the case of the latter, other oils with similar properties should also lead to spontaneous emulsification into monodisperse particle-covered emulsion droplets.

First, mixtures consisting of TMAH-stabilized magnetite dispersions and alkane (octane and dodecane) or cycloalkane (cyclohexane) oils were investigated. Within 24 h the samples did not exhibit the for successful emulsification characteristic turbidity. They remained phase separated with a separate oil phase floating on the dispersion. To enhance emulsification, the samples were gently agitated and then stored without disturbance. After 1 day dynamic light scattering was performed on diluted samples. As expected from the macroscopic appearance, all samples contained polydisperse droplets, indicating a thermodynamically unstable emulsion (Figure 4A). None of these oils can form charged amphiphilic molecules by hydrolysis or dissociation, and surface tensions against water therefore are above 40 mN/m (see Table 1), even in the presence of 6 mM TMAH in the aqueous phase. For comparison, surface tensions of TPM against water and 6 mM aqueous TMAH were measured to be 8.2 and 5.8, respectively. The emulsification failure at such high surface tensions is also in agreement with theoretical predictions.<sup>10</sup> If low surface tensions are caused by hydrolysis of the methoxy groups and subsequent adsorption of the resulting amphiphilic molecule, slower emulsification should occur for (3-methacryloxypropyl)triethoxysilane (MPTES). MPTES has a similar molecular formula as TPM, but with ethoxy instead of methoxy groups. For an overview of molecular structures and chemical properties of the oils employed, please refer to the Supporting Information. Those groups undergo partial hydrolysis much less readily and are therefore an ideal test for the impact of the hydrolysis product on the thermodynamic stability. Indeed, MPTES mixed with TMAH stabilized magnetite suspension did not form stable emulsions within 24 h.



**Figure 4.** Dynamic light scattering (DLS) data showing the radii of the emulsion droplets as a function of the scattering angle. (A) Radii for magnetite stabilized emulsions containing dodecane, octane, and cyclohexane measured 1 day after mixing of the components. Emulsion droplets are polydisperse in all cases. (B) Addition of 10% w/w TPM to the emulsions leads to monodisperse emulsion droplets after 1 day as measured by DLS. (C) DLS data for magnetite stabilized emulsions containing McTMS and McTES. The oil containing methoxy groups, McTMS, forms monodisperse emulsions whereas the ethoxy group containing McTES shows polydisperse droplets.

Surface tension measurement against water and 6 mM aqueous TMAH yielded 19 and 17 mN/m immediately after preparation of the samples. Within 24 h the interfacial tension decreased to 7 mN/m in the presence of TMAH. Yet, no emulsification was observed on the same time scale in the presence of magnetite colloids. This difference may be due to better mixing and therefore a larger contact area between the oil and the water phase during spinning drop measurements which speeds up hydrolysis. This agrees with the significantly larger time of 7 days necessary for spontaneous emulsification.

Further support comes from emulsification experiments with (3-mercaptopropyl)trimethoxysilane (McTMS) and TMAH-stabilized magnetite particles. McTMS is an oil with hydrolyzable trimethoxysilane moiety, but with a mercaptopropyl group as the apolar tail. After 1 day, the mixture showed a significant increase in turbidity and DLS measurements on an unpolymerized sample revealed droplet sizes of 43 nm (Figure 4C). Surface tension between the oil and aqueous TMAH was as low as 3.1 mN/m after 24 h, supporting the correlation between low surface tensions and emulsion stability further. Again exchanging the methoxy for ethoxy groups, that is using (3-mercaptopropyl)-triethoxysilane (McTES) as the oil phase together with TMAH-stabilized magnetite particles did not show increased sample

turbidity. DLS measurements indicated polydisperse droplets, further corroborating the absence of thermodynamic stability (Figure 4C). Even though McTMS can form partially hydrolyzed molecules that exhibit surface-active properties due to the chargeable silane group and the mercaptopropyl tail much faster than the ethoxy variant of the oil, surface tension of McTES in the presence of TMAH was measured to be 3.8 mN/m immediately after mixing. However, within a few hours the sample turned very turbid making surface tension measurements after 24 h impossible.

From the emulsification experiments and surface tension measurements, we conclude that even though low surface tensions play an important role as emulsification was never observed for surface tensions above roughly 10 mN/m, they are in itself not sufficient for stability. The quaternary ammonium ions only have a small effect on the surface tension in the absence of colloidal particles. Surface tensions of alkanes and cyclohexane against aqueous TMAH were slightly lower than against pure water. Yet, only the combination of colloidal particles, quaternary ammonium ions, and the surface-active TPM molecules is sufficient for emulsion stability. We propose that a collective effect between those three components leads to much lower surface tension and therefore stability than is expected from the sum of the individual components. This collective effect is in analogy to significantly lower interfacial tensions achieved by a combination of surfactants and cosurfactants in microemulsions. Theoretical frameworks that find an equilibrium droplet size explicitly consider this adsorption of quaternary ammonium ions at the interface in the single-phase region.<sup>11</sup> Also, in the presence of an excess oil phase this collective effect can be understood as follows:<sup>10</sup> a decrease in the net surface charge by adsorption of the positively charged quaternary ammonium ions allows for further ion dissociation from the colloidal particles. The dissociation yields a gain in ion entropy that can compensate for the more unfavorable oil–water tensions.

Note that the time a bottle of TPM has been opened and therefore exposed to humidity plays a small role in the surface tensions. Surface tension measurements of fresh TPM against water and 6 mM TMAH were found to be 11 mN/m instead of 8.2 and 10 mN/m instead of 5.8 mN/m, respectively. Yet, emulsification was observed with both, indicating that surface tensions around or below 10 mN/m are sufficient to induce spontaneous emulsification in the presence of colloidal particles.

If only the partially hydrolyzed and dissociated molecules are playing a significant role in lowering the surface tensions, then stabilization should also be achieved in the presence of a small number of such molecules that adsorb at the oil–water interface. This can be tested by using oil mixtures of an oil that does not spontaneously emulsify and one that does, for example, TPM.

Therefore, we added 10% w/w TPM to the emulsions containing dodecane, octane, or cyclohexane, agitated the samples gently, and remeasured the droplet size with DLS after 1 day. All droplet sizes became monodisperse and significantly decreased (see Figure 4B). The sample containing an oil mixture of cyclohexane and 10% w/w TPM was remeasured after 4 days. The emulsion droplet size decreased further to 35 nm. Also, a mixture of MPTES and 8% w/w TPM spontaneously emulsified in the presence of magnetite colloids, yielding a droplet size of  $64 \pm 2$  nm by DLS. Emulsion stability for all mixtures of an inert oil and 10% w/w TPM agrees with significantly smaller surface tensions against an aqueous TMAH phase on the order of 10 mN/m (Tables 2 and 3) compared to surface tensions of



**TABLE 2: Interfacial Tensions of Different Oils against Water ( $\gamma_{OW}$ ) or Water Containing 6 mM Salt ( $\gamma_{OW-salt}$ ) Measured Immediately (0 h) and 24 h after Mixing of Oil and Water Phase by a Spinning Drop Tensiometer<sup>a</sup>**

oil phase	$\gamma_{OW}$ (mN/m)	$\gamma_{OW-salt}$ (mN/m)		salt	stable emulsion after 1 day in the presence of colloids?
		0 h	24 h		
cyclohexane	44	42	42	6 mM TMAH	no
dodecane	45	41	41	6 mM TMAH	no
octane	46	45	45	6 mM TMAH	no
TPM (bottle open for 6 months)	8.2	8.5	5.8	6 mM TMAH	yes
TPM (bottle open for 6 months)	8.2	8.5	6.9	6 mM NaOH	no
TPM (new bottle)	11	11	10	6 mM TMAH	yes
TPM (new bottle)	11	11	11	6 mM NaOH	no
MPTES	19	17	7.0	6 mM TMAH	no
McTMS	7.3	7.6	3.1	6 mM TMAH	yes
McTES	3.0	3.8	too turbid	6 mM TMAH	no

<sup>a</sup> To test for spontaneous emulsification, colloidal magnetite was used in all cases except for TPM against NaOH where dialyzed Ludox silica colloids were employed.

**TABLE 3: Interfacial Tensions of Different Oils Plus 10% w/w TPM against Water ( $\gamma_{OW}$ ) or 6 mM Aqueous TMAH ( $\gamma_{OW-TMAH}$ ) Measured Immediately (0 h) and 24 h after Mixing of Oil and Water Phase by a Spinning Drop Tensiometer<sup>a</sup>**

oil phase	$\gamma_{OW}$ (mN/m)		$\gamma_{OW-TMAH}$ (mN/m)		stable emulsion?
	0 h	24 h	0 h	24 h	
cyclohexane/TPM 90/10	18	18	18	9.6	yes
dodecane/TPM 90/10	16	16	11	8.7	yes
octane/TPM 90/10	18	18	11	9.6	yes
MPTES/TPM 90/10	17	15	17	9.8	yes

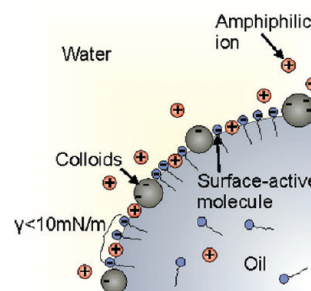
<sup>a</sup> To test for emulsification, colloidal magnetite stabilized with TMAH was used.

the inert oil phase against aqueous TMAH. Without TPM, surface tensions are roughly 45 mN/m for octane, dodecane, and cyclohexane, and 19 mN/m for MPTES. The lower surface tensions and observed spontaneous emulsification into monodisperse droplets clearly link hydrolysis and subsequent dissociation of TPM into surface-active molecules with emulsion stability. However, no stability is achieved in the absence of colloidal particles (see section I). Only a combination of low surface tensions, amphiphilic ions, and colloidal particles yields equilibrium solid-stabilized emulsions. Note also that weak acidity of the oil may be a requirement for the emulsion stability. Strong acids completely dissociate, leading to very low interfacial tensions and probably micellar solutions rather than emulsions. Still, a small quantity of a strong acid may be employed in combination with an inert oil to achieve spontaneous emulsification.

With these minimum requirements in mind, it is straightforward to consider other lipophilic ionizable oils, such as fatty acids, for use as the oil phase in colloiddally stabilized emulsions. Indeed, preliminary experiments on stearic acid and TMAH-stabilized magnetite particles yielded spontaneous emulsification into roughly 150 nm sized droplets as measured by DLS. We are currently investigating the stability of emulsions made from various fatty acids, in analogy with trialkoxysilane-stabilized emulsions.

## V. Conclusions and Outlook

Understanding the basic requirements for stable Pickering emulsions is a stepping stone for the development of mesoscopic equilibrium particle stabilized emulsions. From systematic



**Figure 5.** Schematic of the constituents necessary to achieve thermodynamically stable Pickering emulsions. Adsorption of negatively charged colloidal particles, surface-active molecules, and amphiphilic ions at the oil–water interface leads to stable emulsions.

variations of the main components of a Pickering emulsion, colloids, oil phase, and dissolved ions in the water phase, we have deduced the conditions necessary for spontaneous emulsification into a thermodynamically stable system. Successful oil-in-water emulsion stabilization requires a combination of three conditions: low interfacial tensions between the oil–water interface below 10 mN/m, amphiphilic ions that can adsorb at the droplet interface, and colloidal particles (Figure 5). Stable emulsions were not obtained if one of those components was missing.

In the initial experiments on thermodynamically stable Pickering emulsions, a low interfacial tension was obtained by use of a particular oil (TPM) that hydrolyzes in the presence of quaternary ammonium salts. After dissociation, hydrolyzed TPM is an amphiphilic and therefore surface-active molecule. These molecules adsorb at the interface thereby lowering the interfacial tension significantly. By systematically changing the moieties of TPM, we could attribute emulsification to the hydrolyzable part of the molecules. However, this is just one way of obtaining low interfacial tensions and not required for spontaneous emulsification. Using mixtures of hydrolyzable and inert oils in combination with a hydrolyzing agent and colloidal particles, we obtained stable emulsions for a variety of oil mixtures. As long as both oils mix, the chemical nature of the inert oil is of no influence on emulsion stability. Only interfacial tensions lower than 10 mN/m are required, independent of the chemical composition of the oil, furthermore supported by surface tension measurements on pure and mixed systems. However, low interfacial tensions of the oil–water interface in the absence of colloids are not sufficient for spontaneous emulsification. In theoretical models, even surface tensions below 2–3 mN/m were

required for thermodynamic stability of the emulsions.<sup>10</sup> Emulsion stability also requires the presence of surface-active ions such as quaternary ammonium ions since emulsification was not achieved at low surface tensions in the presence of sodium hydroxide. We therefore suggest that a collective effect of quaternary ammonium ions and colloids leads to a stronger release of counterions. This implies that the presence of colloidal particles yields much lower surface tensions than the oil–aqueous TMAH interface. Furthermore, stabilization is only obtained by negatively charged colloidal particles with a diameter below 203 nm. Possibly the maximum particle diameter with which stabilization still can be obtained is even smaller. Preferential wetting by the oil phase was found to be another common property of colloids achieving stabilization.<sup>25</sup> The detailed nature of the colloidal bulk material is not playing an essential role, as long as the colloidal surface has a preference for the oil phase. It is unclear as of yet whether size and hydrophobicity are only helpful or essential for stable emulsions. Furthermore, it still remains a challenge to make a thermodynamically stable water-in-oil Pickering emulsion. A schematic that summarizes these requirements is shown in Figure 5.

We propose that only the collective effect of adsorption of colloidal particles, low surface tensions, and amphiphilic ions leads to emulsion stability. This general mechanism was found in many different oil–colloid systems, pointing to a new class of equilibrium solid-stabilized emulsions.

The two theoretical frameworks proposed by Zwanikken et al. and Kegel et al. are compatible with the experimental findings in previous work and described in this article. Both models take the basic requirements of low interfacial tensions, amphiphilic ions, and colloidal particles into account while finding an equilibrium droplet radius. Furthermore, they predict a preference of the colloidal particles for the oil phase as well as a maximum colloid size that still induces spontaneous emulsification.

Spontaneous emulsification into particle-stabilized oil-in-water droplets is not only fascinating from an academic viewpoint but may have an impact on emulsion fabrication because of the significant energy savings. The knowledge obtained on the minimum requirements of these Pickering emulsions may be applied to other oils and colloidal particles, with possibly industrial applications in food or material science. Not only oils that create their own surfactants by hydrolysis and dissociation but also oils that achieve similar surface-active molecules in other ways are expected to be used for spontaneous emulsification into particle-stabilized droplets.

**Acknowledgment.** We thank Jos Zwanikken and René van Roij for discussions, and the Dutch Science Organisation (NWO, subsection Chemische Wetenschappen) for funding.

**Supporting Information Available:** Photographs of experimental samples, additional TEM images of emulsions without colloids and with Ludox and Bindzil silica colloids, and plot of droplet size versus oil–colloid mass ratio for TMAH- and TEAH-stabilized magnetite colloids. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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