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ORIGINAL PAPER

Pickering emulsions stabilized by anatase nanoparticles

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Abstract Oil-in-water emulsions can be stabilized by solid particles. These so-called Pickering emulsions are regularly used in many technological applications. Here we describe the efficiency of sol–gel-synthesized anatase nanoparticles with a diameter of 6 nm in stabilizing emulsions. Key parameters were the surface charge of the particles—depending on pH and salt concentration—and their contact angle—depending on the surface groups and the polarity of the oil phase. The effect of these properties on the stability of the emulsions was investigated. The sol–gel nanoparticles were most efficient in stabilizing emulsions at pH 3 (depending on the salt and particle concentration). Highly apolar oil phases (cyclohexane, *n*-hexane) were required to obtain stable emulsions with the investigated system and addition of salt or hydrophobic coupling molecules in the oil phase, such as long alkyl chain containing phosphonates, increased the stability of the emulsions.

Keywords Particle-stabilized emulsion · Titania · Colloids

Introduction

Since Pickering discovered the ability of small particles to stabilize emulsions in 1907 [1], colloidal particles have been an important class of emulsifying agents. The efficiency of such colloids in stabilizing an emulsion depends on a variety of factors. Finkle et al. [2] found that the stability and the type of emulsion that is formed depend on the wetting ability of water and the oil phase for the particles. They stated that a powder must be wetted by both liquids to be able to form an interfacial film, and that the better wetting liquid will form the continuous phase. Schulman and Leja [3] investigated the effect on the type of emulsions of different angles at the oil–water–solid line of contact (Fig. 1). Contact angles were controlled by surface-active compounds. They found that for contact angles slightly below 90°, oil-in-water emulsions were stabilized. However, if the contact angle is slightly >90°, water-in-oil emulsions are stabilized. It was also shown that the contact angle must be near 90° if stable emulsions are to be obtained. Particles that are completely wetted by either water or oil cannot be held at the interface but rather become dispersed in one phase.

Briggs observed that colloidal silica stabilized o/w emulsions whereas carbon black stabilized w/o emulsions [4]. But when appropriate quantities of both compounds were mixed, the resulting mixture did not stabilize any emulsion. He concluded that for stabilization of emulsions the particles need to form a stable interfacial film. For this reason, the particles need to be in a state of incipient flocculation. No emulsion can be formed if the particles are either completely flocculated or completely dispersed [5]. The state of flocculation depends on the interparticle interactions and thus on the surface charge of the particles. As reported by Binks and Lumsdon [6], the stability of emulsions can be controlled by the pH or by addition of electrolytes.

Numerous investigations have been conducted upon emulsions stabilized by silica particles [6–11] including mixtures of hydrophilic and hydrophobic silica particles

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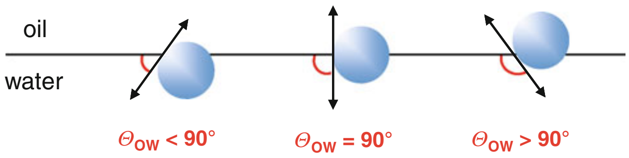

Fig. 1 Oil-water–solid angle of contact

[12]. Different metal oxides [13–16], clay mineral particles [17–20], noble metal particles [21], polymer particles [22–25], and even cellulose fibrils [26, 27] have also been applied for stabilization of emulsions. Moreover, colloidal particles are used to stabilize emulsions in food or cosmetic products. For example, the emulsion state of mayonnaise or margarine was stabilized by lipoprotein particles and fatty acid crystals [28].

Titania nanoparticles have attracted exceptional interest recently because of their unique properties. Using these particles as emulsifying agents can lead to various applications taking advantage of their photocatalytic activity, UV-absorption, good mechanical properties, or the positively charged surface at pH below 6 (contrary to the negatively charged silica surface above pH 2) [29–37]. The most important application of titania particle-stabilized emulsions are in emulsifier-free cosmetics [29, 30], but porous polymer foams also have been prepared utilizing these emulsions [31]. Song et al. [32] used titania nanoparticles not only for stabilization of styrene-in-water emulsions but also, for the first time, for initiation of styrene polymerization by illuminating the emulsions with UV light. The effect of different coating molecules on Pickering emulsions stabilized by commercially available needle-shaped titania pigments were investigated by Stiller et al. [33]. They found that only particles with intermediate hydrophobicity are able to stabilize an emulsion. Pugh studied foams stabilized by anatase nanoparticles [34]. From his studies he concluded that the foaming ability correlates with the surface hydrophobicity, the particle concentration, and the state of dispersion of the particles.

In this paper we describe the optimization of Pickering emulsions stabilized solely by sol–gel-synthesized spherical anatase nanoparticles with 6 nm diameter.

Results and discussion

The crucial properties that affect the stability of Pickering emulsions are the wettability of the particles and the interactions between them. The contact angle is determined by surface properties and by the polarity of the oil phase. The interactions between the particles can be adjusted by varying the pH, electrolytes, and particle concentration. Using sol–gel synthesized anatase nanoparticles, we have investigated the effect of particle concentration, pH, NaCl concentration, solvent polarity, and addition of amphiphilic coupling agents on emulsion stability. The particles were synthesized by a procedure described by Ivanovici [35]. $Ti(O^iPr)_4$ in dry ethanol was added dropwise to ice-cooled water at pH 1.5. Anatase nanoparticles with a diameter of 6(±0.30) nm were obtained.

Emulsions were prepared by addition of 20 vol% cyclohexane, *n*-hexane, or toluene to a 0.5, 1, or 2 wt% suspension of the nanoparticles under agitation with an IKA® T25 Ultra Turrax® disperser. The stability of the emulsions was measured by a procedure developed by Binks and Lumsdon [6]. The emulsions were stored in closed small-diameter vessels and changes of the oil–emulsion and the emulsion–water interfaces were tracked and recorded after specific time intervals. The total volumes of the released oil or water phase can be calculated from the height changes of the interfaces. As seen from Fig. 2, upon creaming the continuous phase is released from the emulsion without destruction of the emulsion droplets. Coalescence on the other hand describes the release of dispersed phase and thus the destruction of the emulsion droplets. The stability to coalescence is described by the amount of released oil phase related to the total amount of oil added. This will be referred to as re-emerged oil phase in the following discussion. By relating the released water phase to the totally added water phase, a value for the stability to creaming is obtained. Figures 3 and 4 show typical pictures of Pickering emulsion stabilized by anatase nanoparticles.

The anatase nanoparticles provide a hydrophilic surface and thus stabilize o/w emulsions. Conductivity measurements of the emulsions proved this assumption by showing high conductivities in the range of several µS/cm to mS/cm for all conditions.

To form a stable interfacial film it is necessary that the particles show interactions with each other without being flocculated. Thus, the surface charge is a very important property for the stability of emulsions. The surface charge can be regulated by adjusting the pH or electrolyte concentration. Figure 5 shows the pH of flocculation for different NaCl and particle concentrations with cyclohexane as the oil phase (if not mentioned differently, cyclohexane is the oil phase for all of the emulsions investigated). The stability of the emulsions is expected to be highest at a pH slightly below the flocculation point.

The critical coagulation points mark the pH where the suspension starts to be non-transparent to visible light, but no sedimentation occurs. The pH of flocculation decreases with increasing salt concentration and with increasing particle concentration (Fig. 5).

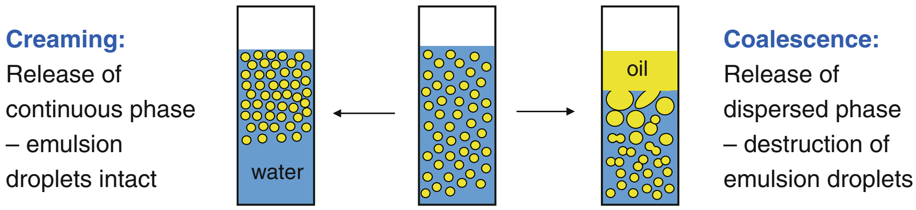

Fig. 2 Stability of emulsions measured by tracking the change of the water–emulsion (creaming) and the emulsion–oil (coalescence) interfaces

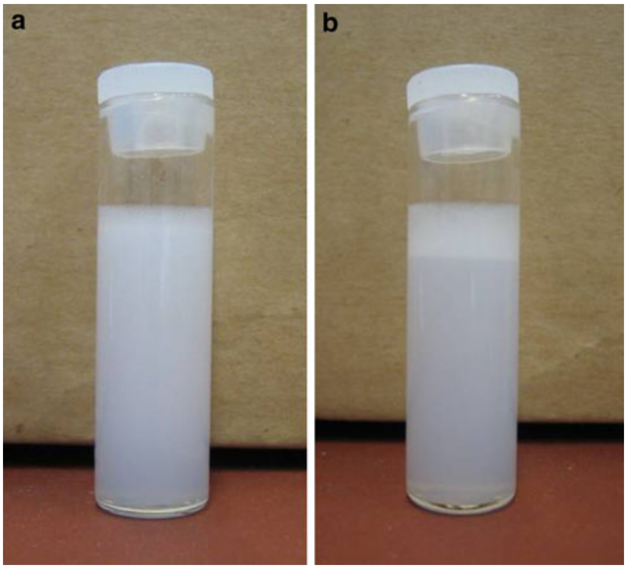

Fig. 3 Picture of a typical emulsion (1 wt% particle concentration, pH 3, no salt, cyclohexane) immediately after agitation (**a**) and 30 min after agitation (**b**)

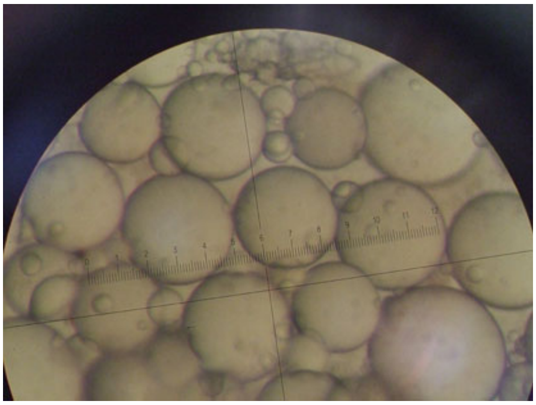

Fig. 4 Optical microscope image of a typical emulsion (1 wt% particle concentration, pH 3, 0.1 M NaCl, cyclohexane)

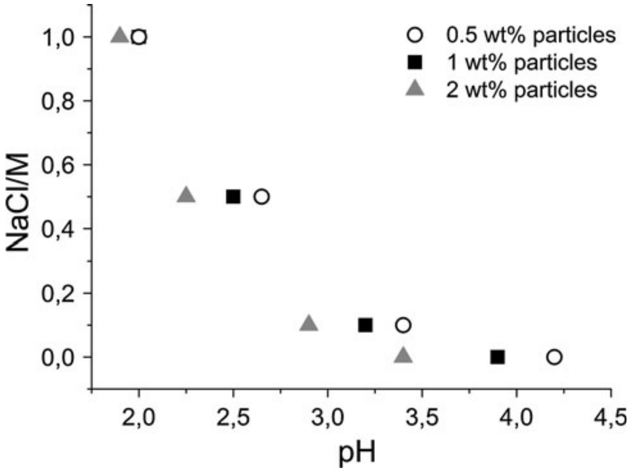

Fig. 5 Critical coagulation pH for different NaCl and particle concentrations

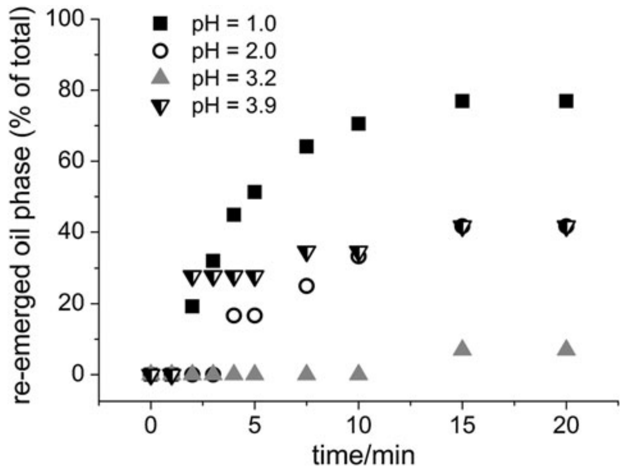

Fig. 6 Stability of emulsions without NaCl and with 1 wt% particles to coalescence depending on the pH: re-emerged oil phase (in % of the totally added oil phase) as a function of time

Figures 6 and 7 show the dependence on pH of the stability to coalescence of emulsions without salt and with 0.1 M salt, respectively. For emulsions without salt, the highest stability was at pH slightly above 3 (3.2), whereas for emulsions with 0.1 M NaCl concentration the highest stability was obtained for pH 2.8. These results are in concordance with the measured flocculation points of suspensions without NaCl (3.9) and with 0.1 M NaCl (3.4). However, the stability of emulsions to coalescence can be increased by addition of salt if the pH is adjusted to the corresponding point of incipient flocculation, which is shifted to lower pH compared with systems without salt. Also investigations on silica particle-stabilized emulsions by Binks and Lumsdon [6] show that addition of electrolytes can enhance the efficiency of the particles in stabilizing emulsions. However, the point of zero charge

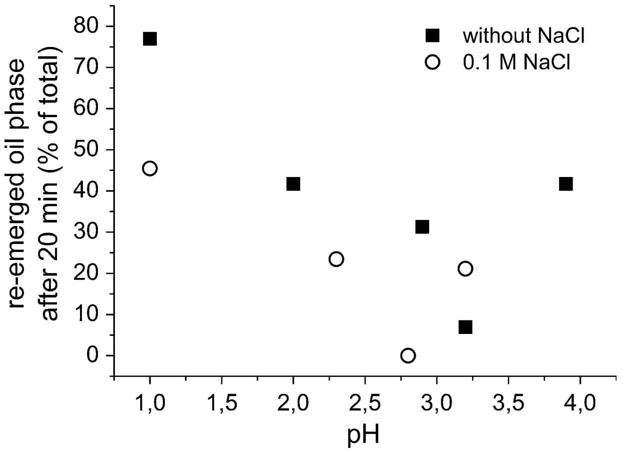

Fig. 7 Stability of emulsions with 1 wt% particles to coalescence depending on the pH and NaCl: re-emerged oil phase (in % of the totally added oil phase) after 20 min

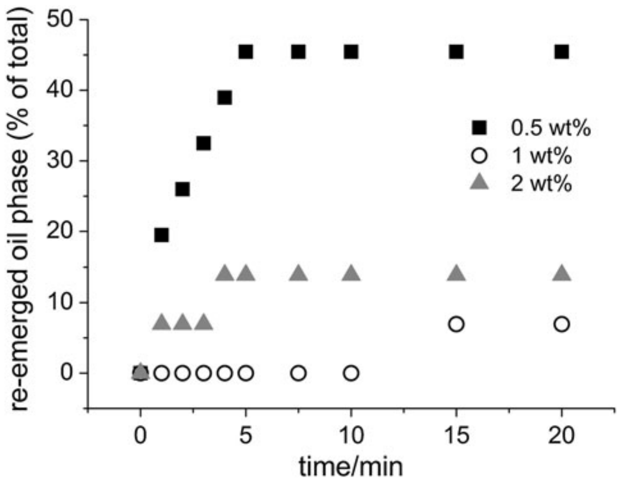

Fig. 8 Stability of emulsions without NaCl to coalescence depending on the particle-concentration: re-emerged oil phase (in % of the totally added oil phase) as a function of time

(pzc) for silica is at pH 2, whereas the pzc for titania is at pH 6. Thus, while the surface charge of silica particles increases with increasing pH starting from pH 2, for titania the surface charge decreases with increasing pH until reaching the pzc at pH 6. Therefore, for silica particles the critical coagulation concentration increases with pH, whereas for the investigated titania particles it decreases. These observations are in agreement with the DLVO theory (developed by Derjaguin, Landau, Verwey, and Overbeek), which combines the effects of the van der Waals attraction and the electrostatic repulsion forces as charged particles approach each other.

Variations in the particle concentration required a new adjustement of the pH for reaching the optimum stability of the prepared emulsions. This is based on the fact that the flocculation point decreases with increasing particle concentration.

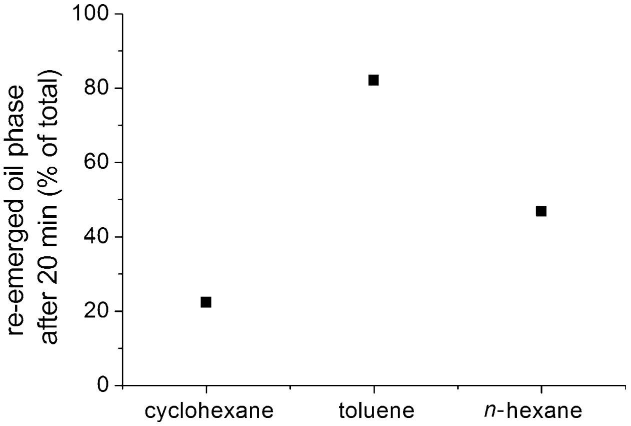

Fig. 9 Dependence on the type of oil phase of the stability to coalescence of emulsions with 1 wt% particles, no salt, and pH 2.9: re-emerged oil phase after 20 min (as a percentage of totally added oil)

The stability to coalescence increases from 0.5 to 1 wt%, but does not increase significantly when elevated over 1 wt% (Fig. 8). Therefore, all subsequent investigations were carried out at 1 wt% of particles.

However, all of the investigated systems were found to be unstable to creaming and the effect of the investigated conditions on the stability to creaming is limited to the induction time. The induction time for both creaming and coalescence is highest at pH 3.2 (without salt) and increases with particle and salt concentration. Similar results were obtained by Binks and Lumsdon [6] in studies on silica particle-stabilized emulsions.

The angle at the oil–water–solid line of contact has a large effect on the stability of Pickering emulsions. Thus, the polarity of the oil phase also plays an important role when the stability of a Pickering emulsion is optimized. For this reason, different oil phases were used and the dependence of the stability of the emulsions on the type of oil phase was investigated (Fig. 9).

Emulsions with highly apolar cyclohexane as the oil phase were found to be more stable than emulsions with the more polar oil phase toluene. This result is in agreement with the investigations of Schulman and Leja [3], who found that the angle at the oil–water–solid line of contact needs to be near 90° to obtain stable emulsions. This contact angle can be adjusted either by controlling the hydrophobicity of the particles' surface or by choosing the oil phase according to its polarity.

An important aspect of particle-stabilized emulsions is their use as reaction environments in the anisotropic surface functionalization of the particles [35]. Addition of hydrophobic coupling agents to the oil phase of the

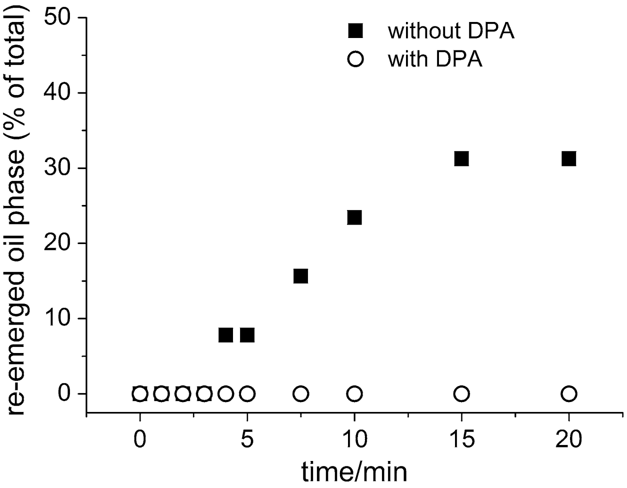

Fig. 10 Stability of emulsions with 1 wt% particles, no salt and pH 2.9 to coalescence, without and with 1.56 mmol/l DPA in cyclohexane: re-emerged oil phase (in % of totally added oil) as a function of time

emulsion provides a straightforward route to Janus-type nanoparticles. Especially, functionalities that react very rapidly with the particles' surface make the particles less mobile and thus increase the stability of the emulsion. For this reason, a proof of principle was carried out for the applicability of these reaction environment for anisotropic surface functionalization of the stabilizing titania nanoparticles by adding dodecylphosphonic acid (DPA) to the oil phase of the emulsion.

The stability of the emulsions increased substantially on addition of DPA (Fig. 10). This result suggests that the particles have a differentiated surface, one hydrophilic and one hydrophobic side.

Summary

The following conclusions can be drawn for Pickering emulsions stabilized by 6 nm anatase nanoparticles:

- the critical coagulation concentration of NaCl decreases with increasing pH, as the surface charge of titania nanoparticles decreases until pH 6 (point of zero charge);
- the most stable emulsions are obtained at pH slightly below the critical coagulation point—where the particles are in a state of incipient flocculation;
- the stability of the emulsions can be elevated by addition of salt to the water phase or hydrophobic coupling molecules to the oil phase;
- the efficiency of anatase particles in stabilizing Pickering emulsions increases with particle concentration—showing a maximum at 1 wt% particles in the water phase; and
- a highly apolar oil phase is required to obtain stable emulsions.

Experimental

Materials and methods

Titanium tetraisopropoxide ($Ti(O^iPr)_4$, 97%, Aldrich), 1-bromododecane (97%, Aldrich), triethyl phosphate (98%, Aldrich) were used as received. Ethanol was dried using magnesium and distilled afterwards.

Operations in which the absence of humidity or oxygen was required were carried out under an argon atmosphere using Schlenk techniques.

Analytical techniques

NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz) equipped with a 5-mm broadband probe head and a *z*-gradient unit. FT-IR spectra were recorded on a Bruker Tensor 27 instrument working in ATR MicroFocusing MVP-QL with a diamond crystal. The software used for analysis was OPUS^{TM} version 4.0. Samples for transmission electron microscopy (TEM) measurements were prepared by ultrasonically dispersing the particles in ethanol before deposition on a carbon-coated TEM Cu grid. TEM measurements were performed on a TECNAI F20 FEGTEM (USTEM, Vienna University of Technology). DLS measurements were performed with an ALV/CGS-3 compact goniometer system with ALV/LSE-5003 light-scattering electronics and multiple τ digital correlator at an angle of 90° and a temperature of 25 °C. The pH was measured using a Mettler Toledo SevenMulti^{TM} meter with saturated KCl glass electrode. The conductivity was determined using a Mettler Toledo SevenMulti^{TM} conductivity meter with Pt/Pt black electrodes.

*Synthesis of anatase nanoparticles (**1**)*
$Ti(O^iPr)_4$ (7.5 cm^3) was dissolved in 25 cm^3 dry ethanol and added dropwise with vigorous stirring to 250 cm^3 distilled water (4 °C) adjusted to pH 1.5 with nitric acid. After 3 days of stirring at room temperature, the solvent was evaporated (40 °C) under reduced pressure. The particles were obtained as a white powder. DLS: 6 ± 0.19 nm; TEM: 6 nm.

*Synthesis of dodecylphosphonic acid (**2**)*
Dodecylphosphonic acid was prepared by the Michealis Arbuzov reaction of 1-bromododecane with triethyl phosphite according to Kosolapoff [38]. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR shifts corresponded to literature data [39].

Preparation of emulsions

In a glass vessel 5 cm high and 1 cm in diameter, 4 cm^3 of a suspension of anatase nanoparticles (**1**) in distilled water (0.5, 1, or 2 wt%) was prepared. The corresponding amount of NaCl (0–1 M) was added and the suspension was adjusted to the requested pH with 1 M NaOH or 1 M HCl. On agitation with an IKA® T25 Ultra Turrax® at 12 rpm, 1 cm^3 oil phase (cyclohexane with or without 1.56 mmol/l DPA, toluene, or hexane) was added dropwise. The emulsion was agitated for another 10 min at 12 rpm. Immediately after stopping the agitation, the conductivity of the emulsions was measured. The water–emulsion and the oil–emulsion interfaces were tracked and the changes were recorded after 1, 2, 3, 4, 5, 7.5, 10, 15, and 20 min.

Separation of particles anisotropically modified with DPA

The emulsions were prepared according to the procedure described above. After measuring the emulsion stability the particles were separated by centrifugation, washed several times with ethanol, and dried under reduced pressure. ^{13}C and ^{31}P MAS NMR shifts and FT-IR signals corresponded to literature data [35].

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