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Encapsulation of Amphoteric Substances in a pH-Sensitive Pickering Emulsion

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Oil-in-water (o/w) Pickering emulsions stabilized with silica nanoparticles were prepared. Droplets of diethyl phthalate (oil phase) act as reservoirs for 8-hydroxyquinoline (8-HQ), which is used as (a) the hydrophobizing agent for the silica particles and (b) an encapsulated corrosion inhibitor for application in active feedback coatings. The hydrophobization of silica nanoparticles with 8-HQ is determined by the amount of this agent adsorbed on the nanoparticle surface. The latter is governed by the 8-HQ concentration in the aqueous phase, which in turn depends on the degree of protonation and finally on the pH. We observe three ranges of 8-HQ adsorption value with respect to nanoparticle hydophobization: (1) insufficient, (2) sufficient, and (3) excessive adsorption by the formation of an 8-HQ bilayer, where only case 2 leads to the necessary nanoparticle hydrophobization. Hence emulsions stable in a narrow pH window between pH 5.5 and 4.4 follow. Here functional molecules are sufficiently charged to compensate for the charges on silica nanoparticles to make them interfacially active and thus able to stabilize an emulsion but they are still to a large extent uncharged and thereby remain in the oil phase. The emulsification is reversible upon changing the pH to a value beyond the stability region.

Introduction

Pickering emulsions[1] are emulsions stabilized by solid particles that adsorb at the water/oil interface due to their ability to be partially wetted by both phases. Interest in these systems has recently increased drastically since it has been discovered how to manipulate and quantify the wetting properties of these particles.

A quantitative measure of this phenomenon is the three-phase contact angle,[2] which determines the energy of attachment to the oil/water interface. The ability of the particles to be wetted more by water than oil supports the formation of oil in water emulsions. Inorganic oxide nanoparticles (e.g., silica, alumina) are of that type and are predominantly dispersible in the aqueous phase due to electrostatic repulsion. But solely hydrophilic particles are poor emulsifiers and cannot prevent coalescence. A suitable surface modification of the particles can render them partially hydrophobic and promote particle flocculation to improve their emulsification capacity. Various attempts to do this have been described in the literature.[3−13]

Binks et al.[5] used silica particles with covalently bonded dimethyldichlorosilane groups on their surface and in doing so varied the number of dissociable silanol groups. The content of silanol groups determines the hydrophilicity of the particles and it was shown that intermediate hydrophobicities allowed quasi-indefinitely stable emulsions. In another work the specific adsorption of trivalent cations[4,9] on negatively charged particles was employed to reduce their effective charge and therefore the hydrophilicity. La^{3+} cations were used for this purpose and it was found that stable emulsions could be prepared with silica particles at La^{3+} concentrations close to the critical flocculation concentration.

The adsorption of ionic surfactants onto oppositely charged particles can synergistically promote emulsification. Here, the hydrophilic head groups act as an anchor for the adsorption and the hydrophobic tails exposed to the surrounding liquid make the particles more hydrophobic. This has been shown for negatively charged particles with cationic surfactants[6,7] and for positively charged particles with anionic surfactants.[3,8,12] For low surfactant concentrations the extent of hydrophobization is intermediate and a large improvement in the stability of oil in water Pickering emulsion is noted. However, high surfactant concentrations can lead to the formation of a surfactant bilayer with the head groups oriented to the water phase rendering the particles again hydrophilic, thereby losing their emulsification ability.[6,8]

A pH-responsive Pickering emulsion was obtained by Li and Stoever[11] by the adsorption of small organic molecules with charged groups but only weak surface activity themselves. The ionic form of potassium hydrogen phthalate (KHP) adsorbs onto positively charged alumina coated silica particles. Due to the protonation of KHP at low pH the adsorption is reversible and the emulsion obtains pH responsive characteristics. Pickering emulsions with pH responsive behavior can also be prepared with bare silica particles at pH values close to the isoelectric point[6,13] by simply lowering the charge of the particles and thereby increasing the hydrophobicity. Another pH responsive emulsion was obtained with poly(4-vinylpyridine)/silica composites[10] which become protonated below pH 4. This effect leads to swelling of the composite, followed by desorption of the particles and the consequent destabilization of the emulsion.

In this work the electrostatically driven adsorption of 8-hydroxyquinoline (8-HQ) onto silica particles (Ludox TMA) is

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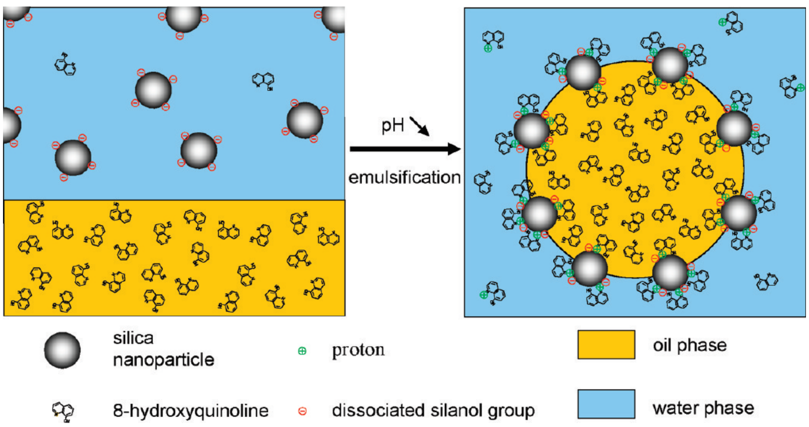
SCHEME 1: **Principle of Lowering the pH Value for Stabilization of o/w Emulsions by Hydrophobized Silica Nanoparticles**[a]



[a] Partitioning of 8-hydroxyquinoline (8-HQ) is mainly in the oil phase for neutral pH, decreasing pH value leads to protonation of 8-HQ, solubilization in the aqueous phase, and simultaneously adsorption onto the silica nanoparticle surface. 8-HQ modified silica nanoparticles then act as emulsifiers for the oil phase.

enabled by the protonation of the nitrogen atom in the aromatic ring (Scheme 1).

This occurs mainly at pH values below 6 and allows the formation of a stable Pickering emulsion under slightly acidic conditions. The novelty here is that 8-HQ acts simultaneously as a component for the hydrophobization of the silica nanoparticles and as an active agent to be encapsulated in the droplets of the oil phase. Because the droplets act as a source of 8-HQ, the concentration in water cannot be adjusted arbitrarily but is determined by the pH value, which controls the partition between water and oil.[14] The prime aim of our study was to form a stable emulsion with the stabilizer, being also a multifunctional molecule with maximum concentration in the oil phase.

Encapsulation of 8-HQ is interesting for example to achieve active feedback metal coatings.[15−20] 8-HQ has features of a corrosion inhibitor for aluminum,[21−23] steel,[24,25] and copper[26] by adsorbing on the metal surface, forming an insoluble chelate complex, and thus blocking the surface for corrosive species. Metal coatings containing nano- or microcapsules with 8-HQ have the potential to prevent corrosion at the damaged sites of the coating by supplying the inhibitor.

It was previously thought that 8-HQ has almost no amphiphilic character itself, but here we showed its ability to form bilayers in the adsorbed state when high concentrations of 8-HQ at a pH value below 4.2 exist in the aqueous phase.

The sparingly water-soluble (1 g/L) compound diethyl phthalate (DEP) was chosen for the oil phase as it provides a high solubility for 8-HQ (1.4 mol/L).

Experimental Section

Materials. DEP, 8-HQ, sodium hydroxide, nitric acid, Ludox TMA (34 wt % Suspension in water) were purchased from Sigma-Aldrich and used without further purification. Water was purified before use in a three-stage Millipore Milli-Q Plus 185 purification system and had a conductivity lower than 18.2 $M\Omega \cdot cm^{-1}$.

Measurement of the Partition of 8-HQ between Water and DEP. An appropriate mass of 8-HQ was dissolved in DEP to prepare a 16.5 wt % solution. The dissolution was accelerated by heating the solution at 60 °C in a water bath. A 1 mL sample of this solution was added to an equal volume of water containing sufficient nitric acid or sodium hydroxide to create a desired pH value in the equilibrium mixture. The emulsion was shaken in a vortex for 12 h and afterward centrifuged at 1000 min^{-1} for 5 min to separate the phases. The pH value of the aqueous phase was determined by using a calibrated glass electrode (SenTix Mic, WTW InoLab). An accurately defined volume of the aqueous phase was then transferred to a volumetric flask containing 10 mM of aqueous HNO_3. The UV−vis spectra of the diluted solution was measured in a UV spectrophotometer (Agilent 8453) and compared with a previously prepared calibration function. The absorbance at the isosbestic point in the spectra at 334 nm was used for calibration and measurement.

Determination of the Adsorption Isotherm of 8-HQ on Silica Particles. Solid 8-HQ crystals were weighed in. The volumes of subsequently added water, Ludox TMA suspension, and diluted HCl were chosen to establish fixed concentrations of 8-HQ in water. In particular the volume of HCl was chosen to guarantee complete dissolution of 8-HQ. The amount of HCl was varied to obtain different pH values. The silica particle concentration was always 300 g/L. The mixtures were then alternately treated in an ultrasonic bath containing water at 50 °C and shaken in a Vortex until complete dissolution of 8-HQ was obtained. After an equilibration time of 12 h (i) the pH value of the suspension was measured and (ii) the particles were centrifuged down at 20 000 min^{-1} for 3 h. The clear supernatant was diluted and measured in the UV spectrophotometer. The difference of the known initial concentration and the measured concentration was taken for the adsorbed 8-HQ amount.

Measurement of Electrophoretic Mobility. Emulsions with 25 vol % DEP (16.5 wt % 8-HQ), 25 g/L Ludox TMA, and sufficient nitric acid to adjust the pH were prepared by shaking for 20 min. The aqueous supernatant after centrifugation for 5 min at 2000 min^{-1} was transferred to a DTS 1060C cell and analyzed in a Malvern ZetaSizer Nano ZS, equipped with a laser operating at 533 nm. The measurement voltage was always 10 V for comparability and to prevent dissolution of the electrodes at high ionic strengths.

Preparation of Emulsions. Ludox TMA suspension, water, 16 wt % 8-HQ in DEP solution, and an appropriate volume of diluted nitric acid to obtain the desired pH value were mixed in a glass vessel. The volumes of Ludox TMA suspension, water, and oil phase were selected to create 25 g/L Silica (related to the aqueous phase) and 25 vol % DEP in 10 mL total volume.

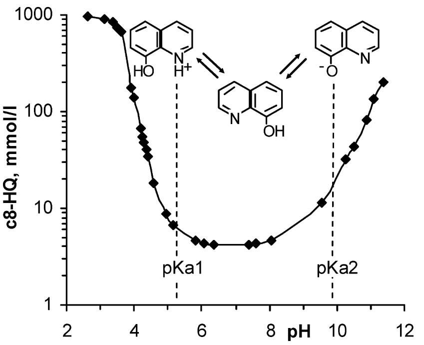


Figure 1. Dependence of 8-HQ concentration in aqueous phase as a function of pH, DEP 50 vol % with initially 16.5 wt % 8-HQ, no silica particles.

The mixture was stirred gently for 1 h to ensure equilibration of the partitioning and adsorption of 8-HQ. The samples were emulsified by treatment for 120 s with an Ultrasonic Processor VCX 505, Sonics & Materials Inc. (20 kHz, 500 W, Newtown, U.S.A.), with a sonotrode tip diameter of 10 mm and an applied power of 40 W. The emulsions were flocculated after the sonication but the flocks could be split into individual droplets by intensive stirring for 5 min.

Quantification of Particle Attachment on DEP/Water Droplet Interface. The separation of excess particles from the emulsion could easily be done by centrifugation at 1000 min^{-1} for 5 min for samples with a low degree of aggregation of the silica particles at pH values above 4.7. The aqueous supernatant of the sample containing the excess particles was then transferred into a glass vessel and dried for 12 h at 80 °C. The dried particles were subjected to a second heat treatment at 500 °C for 6 h to remove all 8-HQ residues. With the initial particle concentration and the known volume of the sample suspension the consumption of particles per oil volume could be calculated.

Measurement of Droplet Size Distribution. A drop of the emulsion was added to a glass slide, covered with a coverslip, and investigated with an optical microscope (Olympus BH-2) operating in dark field mode at a magnification of 400×. Ten micrographs per sample were taken by means of a camera (Olympus C-5050Zoom) with an optical zoom of 5×. The software imageJ was used for the image analysis of the micrographs, employing steps such as contrasting, subtracting background, binarization, and numerical evaluation of droplet cross sectional area. The droplet diameter was calculated and a droplet size distribution was obtained. At least 3000 drops per sample were counted.

Cryo SEM Visualization of Droplet Morphology. The morphology of the concentrated emulsions was examined by high-resolution cryo-scanning electron microscopy (Cryo-SEM). Each sample was cooled by plunging it into nitrogen slush at atmospheric pressure. The samples were freeze-fractured at −150 °C, etched for 60 s at −98 °C, sputtered with platinum in the GATAN Alto 2500 Cryo preparation chamber, and then transferred into the Cryo-SEM.

Results and Discussion

Partition of 8-HQ between Water and DEP. The concentration of 8-HQ in the aqueous phase of a 1:1 (v:v) emulsion containing DEP with initially 16.5 wt % of 8-HQ is represented in Figure 1. 8-HQ has an amphoteric character, hence its water solubility for either acidic or alkaline conditions strongly depends on pH. The pH determines the degrees of protonation of the aromatic nitrogen atom (pK_a = 5.13) and of deprotonation of the hydroxyl group (pK_a = 9.89).[27] In the pH range between these two pK_a values the solubility of 8-HQ is below 10 mM. Albert and Hampton[27] relate this to the internal hydrogen bond between the nitrogen and oxygen atoms, which results in only one center for hydration of the molecule. However, below pH 5 the solubility first increases by 3 orders of magnitude and reaches a plateau of 960 mM at pH 3.

Characterization of Particles

Particle Size and Specific Surface Area. Ludox TMA particles appear almost monodisperse with diameters between 20 and 30 nm (Figure 2a). Results from dynamic light scattering displayed in Figure 2b agree well with the SEM observation and give a narrow size distribution with a maximum at 14 nm and a PDI of 0.05. The calculation of the particle density follows from eq 1

$$\rho_{\mathrm{silica}} = \frac{w}{1/\rho_{\mathrm{H_2O}}(w-1) + 1/\rho_{\mathrm{Ludox}}} = 2.34\ \mathrm{g/mL} \quad (1)$$

where ρ_{Ludox}, $\rho_{\mathrm{H_2O}}$, and w are suspension density, water density, and silica mass fraction in the suspension and their values are 1.24 g/mL, 0.998 g/mL, and 0.34, respectively.

The specific surface area a = 134 m^2/g obtained by BET measurements is in good agreement with the supplier value of 140 m^2/g. Assumption of spherical particles leads to eq 2 that allows the calculation of an average particle diameter d from BET measurements:

$$d = \frac{6}{a\rho_{\mathrm{silica}}} = 19.1\ \mathrm{nm} \quad (2)$$

This particle size was used in any further calculations.

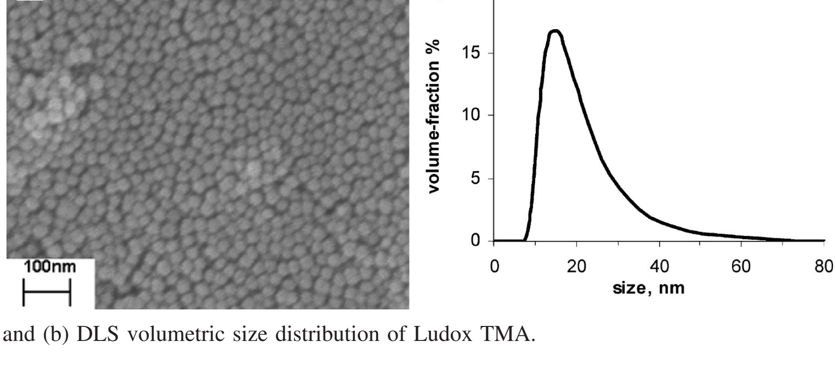


Figure 2. (a) SEM image and (b) DLS volumetric size distribution of Ludox TMA.

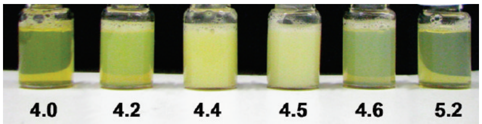


Figure 3. Stability of Ludox TMA with varying pH, concentration of 8-HQ always equals the solubility limit; for pH <4.0 and pH >5.2 the images correspond to those of the extremes.

Adsorption of 8-HQ on SiO_2 Particles. Emulsions prepared in this work always consisted of 16.5 wt % 8-HQ in DEP, water containing the silica particles, and sufficient HNO_3 to obtain the desired pH value. Before the emulsification was done, the two liquid phases were equilibrated by gentle stirring.

This equilibration can be considered as two simultaneously running processes: (i) partition of 8-HQ between both liquid phases and (ii) adsorption of 8-HQ onto silica nanoparticles from the aqueous phase. The final concentration of 8-HQ in the aqueous phase in each particular case is determined by its solubility limit at the corresponding pH as given in Figure 1. This concentration presents an equilibrium value of 8-HQ adsorbed on the silica surface, making also the adsorption−desorption equilibrium pH dependent.

Figure 3 shows a photograph of the silica suspensions with increasing pH value (from left to right) and 8-HQ individual concentrations corresponding to the solubility limit after 2 days (suspensions were shaken before photos were taken). Above pH 4.7 the suspension are clear due to the low light scattering of the nonaggregated silica particles. Between pH 4.7 and 4.3 the suspensions become opaque as a result of aggregation of silica particles, and after several hours sedimentation takes place. Surprisingly, clear suspensions and consequently not aggregated particles can be observed again at pH <4.1. For silica particles alone, only clear suspensions were observed in this pH range.

To understand the reason for this "aggregation window" ζ-potential measurements at different pH values have been performed. The corresponding results are given in Figure 4a. At pH 6, the ζ-potential of bare silica with no 8-HQ present is around -36 mV due to the dissociated silanol groups on the surface. With decreasing pH, protonation of silanol groups takes place, resulting in the decay of the surface charge and consequently a decreasing absolute value of the ζ-potential as shown in Figure 4a. The decay of the absolute ζ-potential is observed to begin at pH 4 and continues until the isoelectric point at a pH of approximately 2.

For the ζ-potential of silica particles in aqueous phase equilibrated with DEP/8-HQ phase a completely different behavior is observed. The absolute value of the ζ-potential already begins to fall at pH 5.5 and the isoelectric point is shifted to pH 4.5. Thus, the aggregation observed in the pH range observed in Figure 3 can be explained in terms of electrostatic destabilization. The ζ-potential can be affected by three processes induced by the gradual pH decrease. First, there is the increased protonation of silanol groups, which also takes place in 8-HQ aqueous solutions. Even stronger charge neutralization can be caused by the electrostatically driven adsorption of positively charged protonated 8-HQ molecules onto the particle surface. The significant increase of 8-HQ solubility, which is also directly related to its protonation as the pH decreases, is the third main factor influencing the ζ-potential of the nanoparticles via an increase in ionic strength and an associated decrease of Debye length. The decreasing pH up to the isoelectric point is accompanied by an increase of the 8-HQ concentration to 20 mM and the conductivity reaches up to 2 mS/cm.

Below pH 4.5 the ζ-potential increases to $+12$ mV. The explanation for this effect could be the formation of 8-HQ bi- or multilayers on the silica surface with the protonated and positively charged nitrogen atom in the aromatic ring of 8-HQ directed toward the solution as shown in Scheme 2.

Bilayers are well-known for phospholipids in liposomes or even adsorbed surfactants on the solid substrate.[28] Hydrophobic interactions of alkyl chains enable the formation of such structures whereas here the interaction of the overlapping aromatic rings, e.g. $\pi-\pi$ stacking or van der Waals attraction, could be suggested as a driving force. This special configuration is possible for this small molecule as a consequence of the localization of polar groups on one side of the molecule. In a bilayer system with charged groups oriented to the solution one would expect a higher ζ-potential. We explain the relatively low ζ-potential of $+12$ mV below pH 4 due to influence of the high ionic strength of the solution on results of ζ-potential measurements (conductivity 7 mS/cm at pH 4).

The adsorbed amount of 8-HQ on silica for fixed 8-HQ concentrations vs the pH value is shown in Figure 4b. For the comparably low concentration of 10 mM (corresponding to the solubility at pH 5) the adsorbed amount decreased gradually with decreasing pH. This decay can be explained by the decreasing silanol group dissociation on the surface of the silica particles, which effectively reduces the amount of negatively charged adsorption sites. An increase of the 8-HQ concentration up to 25 mM (corresponding to the solubility at pH 4.5) results in (i) a significant increase in adsorbed amount and (ii) an increased gradient of the adsorption curve above pH 4.25. This change possibly indicates the formation of an 8-HQ bilayer, as

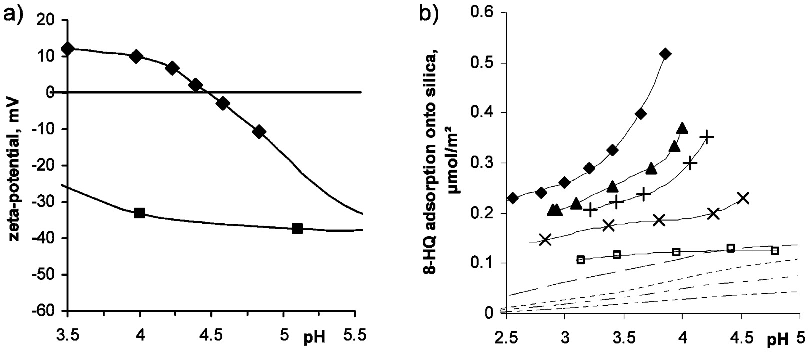
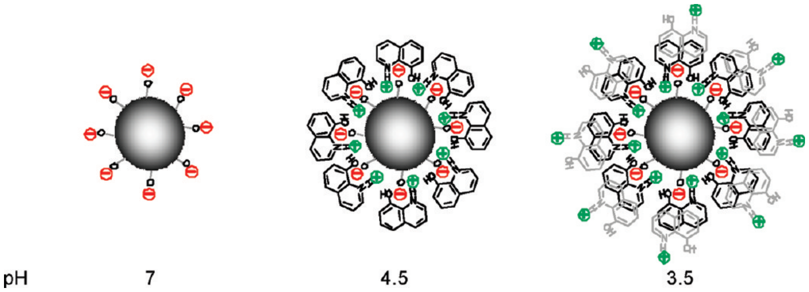


Figure 4. (a) ζ-potential dependence of Ludox TMA silica nanoparticles on pH in water (■) and in aqueous 8-HQ solution corresponding to its solubility limit (◆). (b) Adsorbed amount of 8-HQ per silica surface area vs pH for different 8-HQ concentrations in water: 10 mM (□), 25 mM (×), 50 mM (+), 100 mM (▲), and 250 mM (◆); dashed lines represent data from ref 33 for different 8-HQ concentrations: from the bottom up 1.2, 2.4, 4.8, and 9.5 mM.

SCHEME 2: Model for the Adsorption of 8-HQ onto Silica Particles for Different pH Values[a]



[a] At neutral pH only small fractions of 8-hydroxyquinoline (8-HQ) are dissolved and protonated leading to negligible adsorbed amount on the silica nanoparticle surface. Higher concentration and protonated fraction of 8-HQ at pH 4.5 result in the formation of an 8-HQ monolayer, whereas at pH 3.5 the very high 8-HQ concentration supports the formation of an 8-HQ bilayer onto the silica nanoparticle surface.

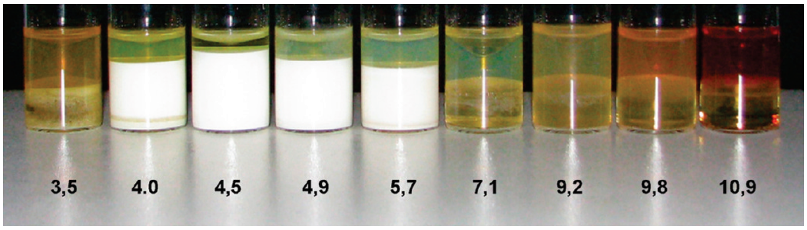


Figure 5. Emulsions of 50 vol % DEP (16.5 wt % 8-HQ) in water for different pH values after 2 weeks (pH value denoted below the vessels). The white sediment corresponds to the emulsified DEP phase. The upper clear (or slightly turbid) liquid corresponds to the aqueous phase, whereby the color ranging from yellow to orange corresponds to the 8-HQ concentration.

depicted in Scheme 2, in line with the reversal of the sign of the ζ-potential seen in Figure 4. The increased gradient of the adsorption curve can still be considered as an effect of the change of the silica charge density with pH. With a decrease in pH, electrostatically adsorbed 8-HQ molecules desorb alongside their associated molecules, increasing the rate of desorption.

With further increasing concentration of 8-HQ the adsorbed amount increases drastically. Also the increase of the gradient in the adsorption curves becomes more pronounced, thereby indicating increasing association between 8-HQ molecules in the adsorption layer. The last points on the right-hand sides of the curves represent approximately the adsorbed amounts for 8-HQ saturated solutions so that connecting them can give an idea how the 8-HQ adsorption behaves for the shown ζ-potential dependency in Figure 4a. The BET isotherm model considers multilayered adsorption and gave, applied to the adsorption data of 8-HQ on silica, a reasonable fit (Supporting Information).

A comparison of the average areas for one adsorbed 8-HQ molecule and one dissociated silanol group could give further information about the adsorption behavior. Unfortunately the published data for the silica charge density vary by orders of magnitude. In 8-HQ saturated water at pH 5 (monolayer region) with about 10 mM dissolved 8-HQ an average area per 8-HQ molecule of 13 nm^2 can be calculated from the adsorption measurements. Data from Tadros[29] give an average area of about 7.6 nm^2 (21 μC/m^2 in 10 mM KCl) and data from Bolt[30] about 44.5 nm^2 (3.6 μC/m^2 in 10 mM NaCl) per dissociated silanol group at this pH value. Most authors[31,32] report values similar to the data of Bolt. The comparison of the two average silanol group areas with the 8-HQ adsorption area gives in the first case less and in the second case more adsorbed 8-HQ molecules than dissociated silanol groups. Adsorption here might not only be driven by electrostatics as also about 50% of the dissolved 8-HQ molecules are uncharged at this pH value (Supporting Information). Then also with the low charge density from Bolt's measurements sufficient adsorption sites can be available. However, this is not the case at pH 4 where more than 90% of 8-HQ are dissociated and the adsorbed 8-HQ amount in a 10 mM solution is only slightly lower. Although the charge density of silica tends to be lowered due to the smaller pH value, the presence of 8-HQ might increase the charge density as is the case in the presence of tetraethylammonium chloride cations[29] for pH values below 6. Further studies involving potentiometric titrations could help us to understand more about the adsorption mechanism.

Comparing the adsorption curve of this work at 10 mM 8-HQ with the adsorption curve obtained by Ferreiro and Bussetti[33] at 9.5 mM onto silica gel shows good agreement above pH 4. However, with pH decreasing below pH 4 the adsorption onto silica gel shows a stronger decrease. A possible explanation might be a different charge density dependency on pH for silica gel.

Characterization of Emulsions under Varying pH. The appearance of DEP emulsions in water containing 16.5 wt % 8-HQ and stabilized by 25 g/L Ludox TMA at different pH values is shown in Figure 5. Above pH 7 emulsions coalesce rapidly forming a lower clear DEP and an upper clear water phase. Silanol groups are mainly negatively charged rendering the particles hydrophilic. Between pH 7 and 9 the concentration of 8-HQ in water is below 4 mM and the protonated fraction is negligible. The amount of 8-HQ adsorbed on the silica nanoparticles should therefore be small in this region. Above pH 9 the concentration of 8-HQ increases rapidly but only negatively charged molecules with deprotonated hydroxyl groups are dissolved in the aqueous phase. Electrostatic repulsion between these and the silica surface disfavors adsorption in this case.

Emulsions show long-term stability between pH 4 and 5. As shown in Figure 4a, the ζ-potential of the silica particles possesses values between −10 and +10 mV in this pH range as a result of the 8-HQ adsorption and high ionic strength. The particles are weakly flocculated, more hydrophobic, and therefore able to act as emulsifiers. From pH 5 to 4.4, the sediment height increases. According to Figure 3 in this pH range pronounced aggregation of silica particles occurs. Consequently, the sediment contains not only emulsion droplets stabilized by silica but also aggregates made exclusively of silica particles.

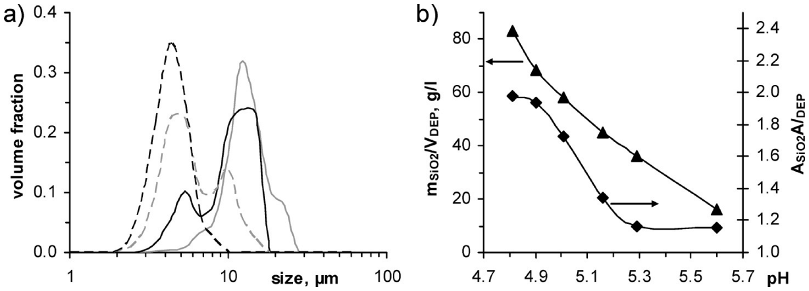


Figure 6. (a) Volumetric size distribution of DEP droplets for different pH values (key to lines: gray continuous, pH 5.6; black continuous, pH 5.3; gray dashed, pH 5.1; black dashed, pH 4.8). (b) Amount of silica nanoparticles attached onto the DEP/water interface as a function of pH. Left ordinate: mass per oil volume (▲). Right ordinate: apparent silica cross section area per total interfacial area (◆). A_{SiO_2} corresponds to total equatorial cross section area of all attached 20 nm spheres; $A_{Interface}$ corresponds to total interfacial area of DEP droplets according to the size distribution in part a.

Below pH 4 again, only unstable emulsions can be formed revealing coalescence after minutes. This could be explained by the already discussed bilayer formation. In this case the hydrophilic groups of 8-HQ are oriented toward the aqueous phase, enhancing the hydrophilic character of the particles.

Figure 6a shows volumetric droplet size distributions for different pH values. At pH 5.6, the monomodal distribution (maximum of 12 μm) changes, via bimodal distributions, to another monomodal distribution (pH 4.8, maximum 4 μm). Under mechanical stress (e.g., stirring, centrifugation) 12 μm droplets at pH 5.6 can release DEP and coalesce to bigger droplets. However, 4 μm droplets formed below pH 5 are very stable and can survive centrifugations at RCF ≥ 1000.

To determine the silica amount required for the emulsification of a given oil volume, measurements based on the mass balance for the silica particles were done. The results for different pH values are displayed in Figure 6b and show a steadily increasing amount of silica from pH 5.6 to 4.8. This can be attributed to the higher demand of particles due to decreasing size of the emulsion droplets and correspondingly due to the increasing interfacial area (Figure 6a). To allow for this effect, the particle attachment is also displayed in terms of total cross section area of attached silica spheres per total interfacial area of the emulsion. For the case where the ratio equals unity, monolayer coverage of emulsion droplets by particles is observed. However, even at pH values above 5.3 more than a monolayer seems to exist on the droplet surface. This observation and the increase of the ratio up to a double monolayer value at pH 4.8 can be attributed to aggregated particle domains on the droplet surface. Below pH 4.8 the requirements of our experimental strategy are not fulfilled because particle aggregation takes place and impedes the separation of droplets and excess particles.

To visualize the droplets shell morphology and to obtain further insights into particle attachment in the pH range below pH 4.8 (Figure 6b), Cryo SEM measurements were performed. The images of Figure 7a at pH 4.7 clearly show aggregated silica structures on the droplet surface, which are postulated from the particle attachment curve in Figure 6b. For pH 4.5 (Figure 7b), the same effect can be observed but with a slightly lower extent. Droplets at pH 4.2 (Figure 7c) show incomplete monolayer coverage with some unoccupied regions on the DEP/water interface. Here, the particle hydrophobicity is already insufficient due to the formation of an 8-HQ bilayer and particles begin to repel each other. Hence, the particle attachment curve can be extended at least in qualitative terms. After reaching a maximum between pH 4.8 and 4.5 the amount of attached silica per DEP volume decreases again and the ratio $A_{SiO_2}/A_{interface}$ decreases below unity slightly above pH 4.2.

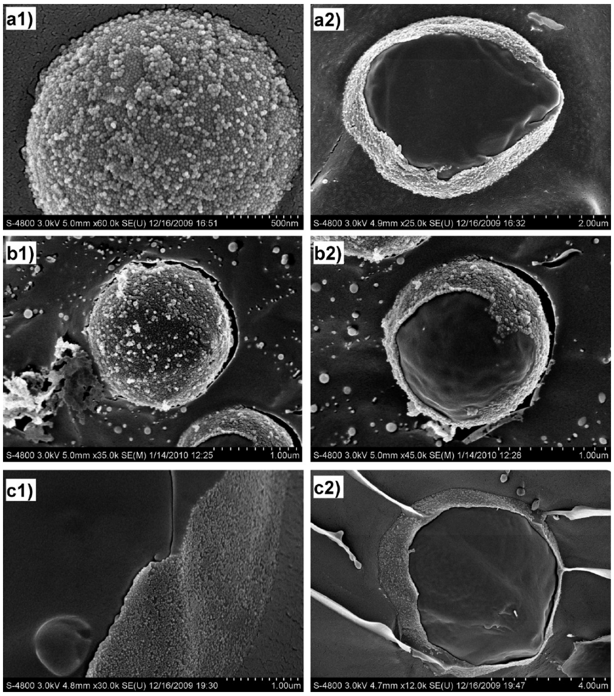


Figure 7. Cryo SEM images of silica stabilized DEP droplets (16,5 wt % 8-HQ) at (a1, a2) pH 4.7, (b1, b2) pH 4.5, and (c1, c2) pH 4.2; cross-section views of droplets are a consequence of the freeze fracture sample preparation.

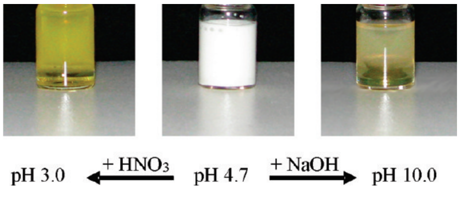


Figure 8. Destabilization of a stable emulsion by adding either acid or base.

Our work explores the pH window in which an emulsion stabilized by silica particles can be prepared. The formed emulsions are stable for at least 6 months (for pH 4.5) of laboratory storage without any observation of coalescence. Another important question is whether the destabilization of a stable emulsion can be trigger by change in pH. Figure 8 shows that upon addition of strong acid or base in amounts sufficient to shift the pH value significantly our stable emulsion can be destabilized and the formation of two separate phases (DEP and water) is observed. This process does not occur immediately, but after stirring for 1 h both separated phases are obtained.

The release of 8-HQ at different pH values in water occurs in less than 1 min (Supporting Information).

Conclusions

Stable o/w-Pickering emulsions with a core consisting of diethyl phthalate containing 8-hydroxyquinoline (8-HQ) stabilized by 20 nm Ludox TMA particles are obtained in a narrow pH range. The stabilizing mechanism is based on the adsorption of 8-HQ on the surface of silica nanoparticles rendering them hydrophobic and therefore more interfacially active. The study revealed the optimum pH range for the stability of the emulsion to be between 4.4 and 5.5. Here high emulsion stability is observed with a maximum remaining concentration of 8-HQ in the emulsion droplets and a minimum droplet size. Above pH 5.5, insufficient adsorption of 8-HQ results in unstable emulsions whereas below pH 4.4 the formation of an 8-HQ bilayer on the particle surface and rehydrophilization are responsible for emulsion destabilization.

Hence we achieved a situation where the particle is sufficiently hydrophobic due to molecule attachement, but the functional molecule is to a large extent uncharged to reside predominantly in the oil phase (Scheme 1).

The median droplet size for stable emulsions is shifted from 12 μm at pH 5.6 to 4 μm at the lower pH. For stable emulsions, solid shells around droplets are formed by densely attached particles revealing also some aggregated domains. The stability of emulsions can be broken by addition of either acid or base.

The emulsions containing about 16 wt % of encapsulated corrosion inhibitor 8-HQ can act as a release system. For future study, the embedding of the particle stabilized droplets into a water-based metal coating and tests of the anticorrosive properties of this system are scheduled.

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Supporting Information Available: Dissociation behavior of 8-HQ, adsorption isotherms of 8-HQ on silica, dynamic light scattering of silica particles in saturated 8-HQ solutions, and release kinetics of 8-HQ from an emulsion. This material is available free of charge via the Internet at http://pubs.acs.org.

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