Pickering emulsions stabilized by hydrophilic nanoparticles: *in situ* surface modification by oil

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Abstract

We propose a novel route for the stabilization of oil-in-water Pickering emulsions using inherently hydrophilic nanoparticles. In the case of dialkyl adipate oils, *in situ* hydrophobisation of the particles by dissolved oil molecules in the aqueous phase enables stable emulsions to be formed. Emulsion stability is enhanced upon decreasing the chain length of the oil due to its increased solubility in the precursor aqueous phase. The oil thus acts like a surfactant in this respect in which hydrogen bonds form between the carbonyl group of the ester oil and the hydroxyl group on particle surfaces. The particles chosen include both fumed and precipitated anionic silica and cationic zirconia. Complementary experiments including relevant oil-water-solid contact angles and infra-red analysis of dried particles after contact with oil support the proposed mechanism.

Introduction

Adipate esters, of general formula ROOC-$(CH_2)_4$-COOR, are synthesized from adipic acid and different alcohols and are a commonly-used ingredient in plastic products, cosmetics and pharmaceuticals.[1] In the latter two categories, they are used as the oil phase of a thermodynamically unstable emulsion, requiring the inclusion of an emulsifier to facilitate emulsification and enhance the kinetic stability of the formed emulsion. Solid colloidal particles can be used in place of molecular surfactants to impart kinetic stability to these systems.[2,3] Their emulsifier-free character makes them attractive regarding applications where surfactants have detrimental effects, in particular when contacted with living matter for body care and health applications. However, little is documented on emulsions of adipate esters.

The mechanism of Pickering emulsion stabilisation has been researched extensively.[2-8] Under conditions where the particles are adsorbed strongly at the oil–water interface, a layer of particles is formed around the drops which sterically hinders the close approach of drops, thus stabilizing them against coalescence. One key parameter controlling the type and stability of solid-stabilized emulsions is the wettability of the particles attached to the oil–water interface.[7,8] As a mimic of surfactants, particles of intermediate wettability were shown to be the most effective emulsifiers. This is quantified for spherical particles through the three-phase contact angle θ normally measured through the aqueous phase. The change in free energy accompanying desorption of a spherical particle from the oil−water interface to either bulk phase is given by[8]

$$\Delta E = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2 \qquad (1)$$

in which r is the particle radius, γ_{ow} is the bare oil−water interfacial tension and the plus sign refers to desorption into oil whereas the minus sign refers to that into water. Values of ΔE for sub-micron particles at oil-water interfaces are typically orders of magnitude greater than the thermal energy of a particle such that particles can be envisaged as irreversibly bound to the fluid interface.

A variety of particles has so far been studied as emulsion stabilizer, including synthetic polymer particles and a range of inorganic particles. By changing the type of monomer and co-monomer, polymeric particles can be endowed with favorable surface characteristics.[9,10] Unfortunately, any residual impurities (monomer, initiator, cross-linker) make such particles ill suited for health and body care applications. On this, inorganic silica particles are a better alternative even though they are very hydrophilic and unfavorable for the emulsification of non-polar oil. To modify silica, surface silylation by dichlorodimethylsilane or silane coupling reagent is extensively used[11,12] although these processes are not environmentally friendly because hydrogen chloride is generated or acid/base is employed. Furthermore, the residue of hydrochloride or base in the products can deteriorate the quality of the particles. Another strategy, addition of a surfactant or polymer referred to as *in situ* surface activation, is employed to enhance the inefficient stabilization of bare silica[13-16], but the emulsifier-free character is lost in such cases. Therefore, use of bare silica particles as a sole stabilizer instead of hydrophobized silica may be of interest from a formulation point of view, such as replacing environmentally problematic surfactants in home and personal care products or E-number registered ingredients in food formulations.

So far, some attempts have been focused on the stabilization of oil-in-water (o/w) emulsions with bare silica particles. Typically, bare silica yielded emulsions of poor stability that rapidly creamed and coalesced when a non-polar oil was chosen.[16,17] Also, it was reported that weak flocculation of silica by multivalent electrolytes, *e.g.* $CaCl_2$, $LaCl_3$, promotes adsorption to the oil–water interface and causes temporary improvement in emulsion stability.[9,17-19] Stabilization of o/w Pickering emulsions by completely hydrophilic silica nanoparticles was successful however upon selection of favorable oils and increasing the oil phase polarity was found to improve emulsion stability.[17,20,21] For example, Frelichowska *et al.*[20] emulsified oils such as butanol, ethyl acetate and butyl lactate successfully, but complete phase separation was observed immediately after emulsification when emulsifying other oils like diethylhexyl succinate and octyl benzoate. No explanation was put forward to explain this difference however. It may be that the extent to which hydrophilic particles are wet by polar oils is greater than that by non-polar oils.

Here, we investigate the aqueous phase behavior of a range of hydrophilic particles in the presence of adipate esters and the subsequent emulsions formed from their mixture. We suggest a new mechanism by which inherently hydrophilic particles can be surface activated by adsorption of oil molecules. This activation is crucially dependent on the water solubility of the oil which can be varied by varying the chain length of the R group in the diester.

Experimental

Materials

Three types of hydrophilic particles were used. The amorphous fumed hydrophilic silica powder (HDK N20, 100% SiOH, Wacker–Chemie) was made up of primary particles with diameters of between 5 and 30 nm. During synthesis and storage, the primary particles show a strong tendency to build up into aggregates with diameters of several hundred nm.[6] Highly negatively charged Ludox HS-30 silica sol was received from Grace Davison as a 31.6 wt.% aqueous dispersion at a high pH of 9.8. The mean particle diameter was determined to be 15 nm.[22] Highly positively charged colloidal zirconia sol was received from Nyacol Nano Technologies Inc. as a 20 wt.% aqueous dispersion at a low pH of 1.7. The mean particle diameter is 5-10 nm provided by the manufacturer. Dodecane (99%), diethyl adipate (99%) and dibutyl adipate (96%) were purchased from Sigma-Aldrich (UK). Dimethyl adipate (99+%) and bis(2-ethylhexyl) adipate (99.0%) were purchased from Acros Organics (UK). Dipropyl adipate (99+%) was purchased from TCI Chemistry (Japan). The densities of the adipates are given in Table 1. All oils were columned through neutral chromatographic alumina (stage 1, 70-230 mesh, Mech KGam) to remove polar impurities. Ultrapure water of resistivity 16 MΩ cm and pH 6.0 was obtained from a Milli-Q reagent water system connected to an Elga reverse osmosis unit.

Methods

(a) *Solubility of adipate oil in water*

In order to determine the solubility of the different adipate oils in water at 20 °C, a known amount of oil was weighed into a glass vessel followed by addition of water (typically 250 mL) with extensive shaking. If the oil was not dissolved completely (oil droplet or turbid solution visible), a known amount of water was added with shaking until a transparent solution was obtained. Knowing the total volumes of oil and water added, the solubility was calculated.

(b) *Zeta potential of N20 silica particles in aqueous solutions of dimethyl adipate*

The zeta potentials of N20 silica particles dispersed in aqueous solutions of dimethyl adipate were obtained using a Malvern Zetasizer Nano-ZS instrument. The Smoluchowski equation was used to convert the measured electrophoretic mobilities into the corresponding zeta potentials. Samples were prepared by dispersing 20 mg of silica particles into 20 mL of aqueous dimethyl adipate solution ultrasonically for 2 min. An average value of the zeta potential is reported for 5 consecutive measurements of the same sample at 25 °C.

(c) *Surface tension of aqueous adipate solution*

The air-water surface tensions of aqueous dimethyl adipate solutions of different concentration were measured using a Krüss K12 digital tensiometer thermostated at 25 °C employing a Pt plate. All vessels were rinsed in alcoholic KOH and then Milli-Q water before use.

(d) *Contact angles at hydrophilic glass–oil–water interfaces*

The advancing contact angles θ (through aqueous phase) at the hydrophilic glass - oil-water interface were measured using a Krüss Drop Shape Analyser 10 instrument. The glass microscope slides were rendered completely hydrophilic ($\theta < 4^{\circ}$ for a water drop in air) by immersing them in 30% aqueous KOH for two hours, rinsing in ultrapure water followed by drying at 110 °C in a drying cabinet. For adipates denser than water,

water and adipate oil were mixed thoroughly beforehand to ensure mutual saturation. For contact angle measurement, a glass cuvette was partly filled with adipate-saturated water and a water-saturated adipate oil drop (5 µL) was formed under it on the substrate. For dodecane and adipates which are less dense than water, an oil-saturated water droplet was placed on the slide and the cuvette was then filled with water-saturated oil. The contact angle at the hydrophilic glass-dodecane-aqueous dimethyl adipate interface was measured by a similar method. A drop of aqueous dimethyl adipate was formed on the substrate and the cuvette was then filled with dodecane. Here, the oil and aqueous phases were not in contact before measurement to avoid extracting the dissolved adipate into dodecane.

(e) *Preparation and characterization of emulsions of adipate oils*

N20 silica powder was dispersed in Milli-Q water using a high intensity ultrasonic vibracell processor (Sonics & Materials, 0.3 cm tip diameter) operating at 20 kHz and up to 10 W for 20 min. During sonication, it was necessary to cool the vessel in an ice-bath. Two mL of adipate oil and 8 mL of aqueous silica dispersion were emulsified in a glass vessel (d 1.2 cm, l 7.5 cm) thermostated at 25 °C. Emulsification was achieved with an IKA Ultra Turrax homogenizer fitted with a dispersing head of 8 mm operating at 13,000 rpm for 2 min. The emulsion type was inferred by observing whether a drop of emulsion dispersed or remained when added to either pure oil or pure water. For microscopy, a drop of the emulsion was diluted in its continuous phase on a glass microscope slide and gently covered with a cover slip. Images of emulsion drops were taken using a Nikon Labophot microscope fitted with a DIC-U camera and assisted with the software Image-Pro Plus 5.1 (Media Cybernetics). The average diameter of emulsion droplets was calculated from 100 individual drops. Photographs of the vessels were taken with an Olympus µ670 digital camera. To characterize the stability of an emulsion, the volume of oil released was determined and used to calculate the % released oil relative to that added initially. Besides N20 silica particles, emulsions of adipate oil were stabilized by Ludox HS-30 silica sol and zirconia sol. The two sols were diluted to 1.0 wt.% by water of pH 9.8 and pH 1.7, respectively. Emulsions were prepared and characterized as described above. pH measurements were made with an aqueous glass pH electrode.

(f) *Preparation and characterization of emulsions of dodecane*

In the first protocol, N20 silica particles were dispersed in aqueous adipate solutions of different concentration and used to prepare dodecane-in-water emulsions (particles contact water and adipate molecules simultaneously). To obtain adipate-saturated water, water was thoroughly mixed with adipate oil. After phase separation, the transparent adipate-saturated water was separated. Aqueous adipate solutions of different concentration were prepared by diluting the saturated solution. 1 wt.% of N20 silica particles was dispersed ultrasonically into these solutions. Finally, 8 mL of this aqueous dispersion and 2 mL of dodecane were emulsified and characterized as above. In the second protocol (particles contact water first and then dissolved adipate molecules), adipate-in-water emulsions containing 1 wt.% of N20 silica particles and $\phi_o = 0.02$ were prepared. Such a low oil volume fraction means that the particle content in the released water after creaming is also around 1 wt.%. 8 mL of this released water and 2 mL of dodecane are emulsified as described above.

(g) *Infra-red analysis of dried aqueous phase in adipate-in-water emulsion*

Emulsions of different adipate oils were prepared at a silica particle content of 1 wt.% and oil volume fraction of 0.2. After creaming/sedimentation, the emulsion was removed by pipette and the silica particles in the drained water were separated by centrifugation at 6,000 rpm. The wet silica sediment was dried at 110 °C in a drying cabinet to constant weight. The infra-red spectrum of the obtained silica powder was measured using the KBr tablet method on a PerkinElmer Spectrum RX1 spectrometer. The absorbance at 473 cm^{-1} was maintained around 0.5 by adjusting the amount of powder carefully. The ratio of the absorbance of the C=O group (at 1732 cm^{-1}) to the Si-O-Si group (at 473 cm^{-1}), A_{1732}/A_{473}, was determined and used to compare the relative amount of adipate oil to silica residing in the continuous phase of the emulsions.

Results and discussion

After first determining the solubility of the adipate oils in water, we then describe the behavior of emulsions of these oils with water in the presence of N20 fumed silica particles. Emulsions of dodecane and aqueous dialkyl adipate stabilized by the same particles are then discussed alongside complementary experiments of contact angle and adipate oil chemisorption to particle surfaces. Finally, results for the emulsification of the different adipate oils in water in the presence of the other two hydrophilic particle types are given.

(i) Solubility of adipate oils in water

The solubilities in water of five dialkyl adipate oils are given in Table 1. A homologous series of oils in which the number of carbon atoms in each ester moiety (R) increases from 1 to 4 is chosen alongwith an oil containing a branched C_8 chain. Increasing the chain length has a significant effect on the solubility, which falls by a factor of approx. 600 in going from dimethyl adipate to bis(2-ethylhexyl) adipate. The values for the two lowest chain lengths are in good agreement with those in the literature.[23-25] That for diOct is similar to that of hexane in water (0.01 g/L).

(ii) Emulsions of adipate oils stabilised by N20 silica particles

We first verified that emulsions of adipate oil and water (1:1) in the absence of particles phase separated completely soon after emulsification, indicating the oils have no surface-active impurities of any significance. Oil-in-water emulsions containing an oil volume fraction ϕ_o = 0.2 and 1 wt.% of N20 silica particles initially dispersed in water were prepared with all the adipate oils. Figure 1(a) shows their appearance two months after preparation. Since diMe and diEt oils are more dense than water, the emulsion sediments, whereas for the other oils being less dense than water they cream. As a control, we attempted to emulsify dodecane as an example of a non-polar oil incapable of functionalizing particle surfaces. As expected, the mixture exhibited complete phase separation within a few hours. The emulsions of the adipate oils are stable to different extents depending on their chain length. The oils diMe and diEt can be emulsified completely and are stable to coalescence for at least 6 months and 2 months respectively. Following sedimentation, ϕ_o in the emulsion increases to around 0.73, a value close to the minimum internal phase volume fraction of highly concentrated emulsions (0.74).[26,27] The stability of these emulsions arises from the layer of particles adsorbed around droplets. By contrast, the emulsion of diOct phase separated completely in 2 months. Emulsions of diPro and diBut were of intermediate stability showing evidence of significant coalescence. Figure 1(b) shows the variation of the average droplet diameter and the percentage of released oil due to coalescence with silica particle concentration for emulsions of diPro. The inset contains optical microscope images of the emulsions at three particle concentrations. In line with other Pickering emulsion systems, the drop diameter decreases progressively with particle concentration reaching a limiting value of around 45 µm by 6 wt.% particles. Likewise, the stability to coalescence increases markedly. All droplets are spherical and discrete.

Based on these results, we put forward a new mechanism for the activation of hydrophilic particles as emulsion stabilizers in Figure 2(a). Before and during emulsification, polar adipate molecules from the bulk oil phase will dissolve in water up to their solubility limit and may chemisorb on silica particles also dispersed in water. This renders them partially hydrophobic enabling them to adsorb to the oil-water interface and stabilize an o/w emulsion. Oil molecules thus act like a surfactant in this respect. The likelihood of this activation by oil clearly depends on its solubility in water. We plot the coalescence stability of o/w emulsions after 2 weeks or 2 months *versus* the solubility of the adipate oil in water in Figure 2(b). As the chain length of the oil decreases from a total of 22 (diOct) to 8 (diMe), its water solubility increases resulting in improved functionalisation of particle surfaces. Consequently, the stability of the emulsion to coalescence increases markedly, in that 100% oil is released using diOct whilst 0% oil is released using diMe. The experiments which follow were designed to prove our hypothesis.

(iii) Contact angles at hydrophilic glass-adipate oil-water interface

We mentioned earlier that the wetting of particles by water and oil is crucial to their effectiveness in stabilising Pickering emulsions. This can be judged from the contact angle the particle exhibits at the oil-water interface. Since it is very difficult to measure the latter for very small fumed silica particles, we have used a hydrophilic glass slide to represent the surface of these particles and have determined the contact angle at the adipate oil-water interface on such substrates. Oil and water were mutually saturated before measurement. Figure 3(a) shows how the oil-water contact angle measured through water varies with the number of carbon atoms in the adipate oil. It decreases from over 50° for diMe to around 20° for diOct, *i.e.* surfaces become more hydrophobic as the oil chain length decreases. We believe this is mainly due to the adsorption of adipate oil molecules onto the substrate from either oil or water. We correlate the coalescence stability of the o/w emulsions with this contact angle in Figure 3(b). The emulsion becomes increasingly more stable as the contact angle increases. This trend is similar to that observed in systems containing hydrophilic silica particles and increasing concentration of cationic surfactant.[28] In addition, the contact angle at the dodecane-water interface was $< 4°$ implying that the substrate was completely wetted by water. This is consistent with the lack of emulsion stabilization with dodecane for inherently hydrophilic particles.

(iv) Emulsions of dodecane-aqueous diMe stabilized by N20 silica particles

As further confirmation of our hypothesis that high solubility of adipate oil in water results in better stabilization of o/w emulsions, we carried out a series of experiments in which N20 silica particles were first dispersed in water containing different concentrations of dissolved adipate oil (obtained by dilution of a solution at its solubility limit). These aqueous phases were then used to prepare dodecane-in-water emulsions, which as seen above is incapable of yielding a stable emulsion alone. Figure 4(a) shows the appearance of these emulsions immediately after preparation in the case where diMe originates dissolved in water. Clearly, a larger volume of emulsified dodecane can be stabilized upon increasing the adipate oil concentration initially in water. The effect of adipate oil concentration in water on the extent of coalescence is given in Figure 4(b) for different times since preparation. After 42 days, complete phase separation occurs for diMe concentrations ≤ 0.1 g L^{-1} whereas only around 10% of dodecane is released through coalescence at a concentration equal to the solubility limit of 24.0 g L^{-1}. We thus demonstrate that an oil incapable of being emulsified with bare hydrophilic particles can be emulsified once those particles are functionalized by adipate oil molecules dissolved in water. The average dodecane oil drop diameter after 2 weeks is also plotted in Figure 4(b), where it can be seen that it decreases progressively from over 120 μm to below 50 μm on increasing the concentration of diMe in water, in line with the increase in emulsion stability noted above. Similar findings were observed for diEt dissolved initially in water, as shown in Figure 4(c) and (d), with a very stable emulsion being formed at its solubility limit in water.

If we consider the dissolved adipate oil molecules in water as akin to surfactant molecules, various properties of their aqueous solutions should vary with adipate oil concentration. Figure 5 contains data on the variation of air-water surface tension, zeta potential of N20 silica particles in water and contact angle at the hydrophilic glass-dodecane-water interface with the concentration of diMe in water. The surface tension γ decreases with diMe concentration c (in g/L) from 72.0 mN/m for pure water to its limiting value of 40.9 mN/m at the solubility limit demonstrating its surface activity (Figure 5(a)). The shape of the curve is reminiscent of that for short chain alcohols which do not associate in water.[29] The γ-c relationship was fitted to

$$\gamma = 40.8 + 12.3e^{-c/5} \qquad (2)$$

The Gibbs adsorption equation for a nonionic surfactant can be written

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc} \qquad (3)$$

where Γ is the surface concentration of surfactant, R is the gas constant and T is temperature. Although we do not know the activity coefficient of diMe in water, the calculated value of Γ for the saturated solution of diMe in water (0.138 M) at 25 °C is 1.3×10^{-11} mol cm^{-2}. This equates to an area per molecule of diMe of 12.6 nm^2 which is around 15-20 times larger than the saturated area of typical single-chain surfactants. It is likely that the diester assumes orientations which are predominantly parallel to the surface resulting in contact between the chain methylene groups and water, as mentioned previously for the diethyl ester of succinic acid.[29]

Figure 5(b) shows how the zeta potential of N20 silica particles dispersed in aqueous solutions of diMe varies with the concentration of diMe. In pure water, the zeta potential is -33 mV and its magnitude decreases with increasing concentration of diMe, such that at the solubility limit it is close to zero. Such a trend is similar to that of adding a cationic surfactant, where it has been shown that particles of reduced charge are more hydrophobic.[15] This is confirmed with the data in Figure 5(c) for the contact angle of a drop of aqueous diMe under dodecane on a hydrophilic glass substrate, in which the aqueous phase and dodecane were not in contact before measurement. The contact angle increases from around 24° to nearly 37° with increasing concentration of diMe in water. This increase in hydrophobicity relates directly to the progressive improvement in the stability of dodecane-in-water emulsions stabilized by modified N20 silica particles (Figure 4(a)). It is well-known that nonionic surfactants or polymers containing etyhleneoxy (E) groups adsorb on silica surfaces in water *via* hydrogen bonds between the O atom in E groups and the H atom in surface silanol groups.[30] Initially a monolayer is formed rendering surfaces more hydrophobic which can in some cases be followed by completion of a bilayer which makes surfaces hydrophilic again. In one case, the zeta potential of silica microparticles increases from -50 mV to -10 mV with increasing concentration of the surfactant $C_{12}E_8$.[31]

(v) Emulsions of dodecane-aqueous adipate stabilized by N20 silica particles

We wish to understand the reason for the widely differing stability of emulsions of adipate oils in water depending on the chain length of the adipate oil (Figure 2(b)). For this, we conducted two kinds of experiment in emulsifying dodecane. In the first, the aqueous phase released following sedimentation/creaming of an adipate-in-water emulsion was used to prepare emulsions with dodecane *via* homogenisation. Although the particle concentration is expected to be low, the idea is that excess silica particles will be functionalised in water to different extents depending on the solubility of oil in water. The appearance of these emulsions after 2 weeks is seen in Figure 6(a), whilst Figure 6(b) shows how the stability to coalescence during storage varies with the solubility of the adipate oil in water. Again, the emulsion stabilised by silica particles released from a diMe emulsion is the most stable, whilst that from particles released from a diOct emulsion is least stable. In the second, N20 silica particles are dispersed in adipate-saturated water and emulsification with dodecane is performed. The equivalent data are given in Figure 7, where the stability of dodecane emulsions to coalescence increases progressively with the solubility of adipate oil in water.

(vi) Analysis of N20 silica particles after interaction with adipate oil in water

In order to investigate the interaction between molecules of adipate oil and silica particles, we dried the aqueous phase containing particles and oil molecules released from an adipate oil-in-water emulsion and measured the FT-IR spectra of the powdered particles. The spectra are shown in Figure 8 for dried particles originating from emulsions of all the five adipate oils. The peaks at 473 cm^{-1} and 1109 cm^{-1} are attributed to the Si-O-Si bending vibration and the Si-O stretching vibration, respectively. The absorbance at 1732 cm^{-1} is attributed to the C=O stretching vibration within the ester group of the adipate molecules, which is absent for particles dispersed solely in water (spectrum a). For spectra originating from emulsions (b-f), the ratio of the absorbance at 1732 cm^{-1} to that at 473 cm^{-1} (A_{1732}/A_{473}) reflects the relative amount of adsorbed adipate on silica. This ratio is given in Figure 8 where it is seen to increase progressively from diOct to diMe, *i.e*. more adipate oil adsorbs on silica as the oil chain length decreases. It is well known that the carbonyl group of esters interact with silanol (SiOH) groups of silica through hydrogen bonds.[32-34] By increasing the solubility of adipate oil in water (lowering the chain length), more molecules are available for adsorption on silica thus partially hydrophobising them and enabling them to stabilise oil-in-water emulsions.

Since silanol groups deprotonate to SiO$^-$ at high pH, it is expected that the interaction between ester molecules and silica particles will be reduced as a result such that effective particle modification by oil and subsequent emulsion stabilization should be prevented. As proof of this idea, we prepared diPro-in-water emulsions stabilized by N20 silica particles at a range of pH, including the natural pH of 6.0. As shown in Figure 9, the emulsion at pH 9.9 exhibited complete phase separation immediately after emulsification and that at pH 9.1 phase separated just after 2 weeks. Emulsions at pH 2.4 and 3.7 however, where virtually all the SiOH groups are undissociated, exhibit relatively high stability to coalescence for over one month. We verified for dodecane as oil that N20 silica particles were ineffective emulsion stabilizers at all pH between 2 and 10. We thus prove that by losing the favourable interaction between ester molecules and silica particles, no emulsion can be stabilized at high pH which supports our hypothesis that functionalisation of particles by oil molecules is key to emulsion stabilization.

(vii) Emulsions of adipate oils stabilized by other hydrophilic particles

So far we have only presented evidence for the *in situ* functionalisation of N20 fumed silica particles at pH ≤ 6.0. We wanted to establish if this novel approach applied to other hydrophilic particle types, and chose colloidal Ludox HS-30 silica nanoparticles at pH 9.8 and zirconia nanoparticles at pH 1.7. Ludox HS-30 particles are negatively charged at pH 9.8 with a zeta potential value of -43 mV. Since the isoelectric point of aqueous zirconia nanoparticle dispersions is about pH 5.8,[35,36] these particles are positively charged at pH 1.7. Results in the literature show that nonionic sugar surfactants adsorb on cationic alumina particles in water lowering their zeta potential.[37] Oil-in-water emulsions of both dodecane and all the adipate oils were prepared with ϕ_o = 0.2 and with 1 wt.% of particles in water. Their appearance and stability to coalescence after 2 weeks are given in Figure 10, for (a) ZrO_2 particles and (b) Ludox HS-30 particles. Like N20 silica particles, no emulsion is possible with dodecane as oil. The trend in emulsion stability with the chain length of the adipate oil is the same for the three hydrophilic particle types, Figure 10(c). Emulsions completely stable to coalescence form with diMe and diEt whilst coalescence becomes more pronounced in diPro, diBut and eventually diOct. The results indicate that the modification of hydrophilic particles by adsorbed oil molecules is general for different particle types and surface charge.

Conclusions

We show that inherently hydrophilic nanoparticles, incapable of enabling emulsification of dodecane in water, may be rendered partially hydrophobic *in situ* by dissolved oil molecules in the case of dialkyl adipate oils. The important parameter enabling this is the aqueous solubility of the oil. Upon decreasing the oil chain length, its solubility in water increases and stable o/w Pickering emulsions can be prepared. The interaction leading to hydrophobisation is the formation of H-bonds between the carbonyl group of oil molecules and the hydroxyl group on particle surfaces. The generic nature of our findings is demonstrated for three hydrophilic particle types of different charge. It is anticipated that the same phenomenon can be applicable to a range of other oils possessing functional groups and exhibiting limited solubility in water.

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Table 1. Density and solubility in water of different dialkyl adipates at 20 °C.

Oil	Abbreviation	No. of C atoms	Density/ g cm^{-3}	Solubility/± 0.01 g L^{-1}
Dimethyl adipate	diMe	8	1.060	24.00
Diethyl adipate	diEt	10	1.009	4.00
Dipropyl adipate	diPro	12	0.979	0.27
Dibutyl adipate	diBut	14	0.962	0.10
Bis(2-ethylhexyl) adipate	diOct	22	0.930	0.04

Figure 1. (a) Photos of vessels containing mixtures of oil (given), $\phi_o = 0.2$, and aqueous N20 silica dispersion (1 wt.%) two months after emulsification, (b) variation of average oil droplet diameter (squares) and percentage of released oil (circles) with silica particle concentration in water for emulsions of diPro; inset shows microscope images, scale bar = 200 μm.

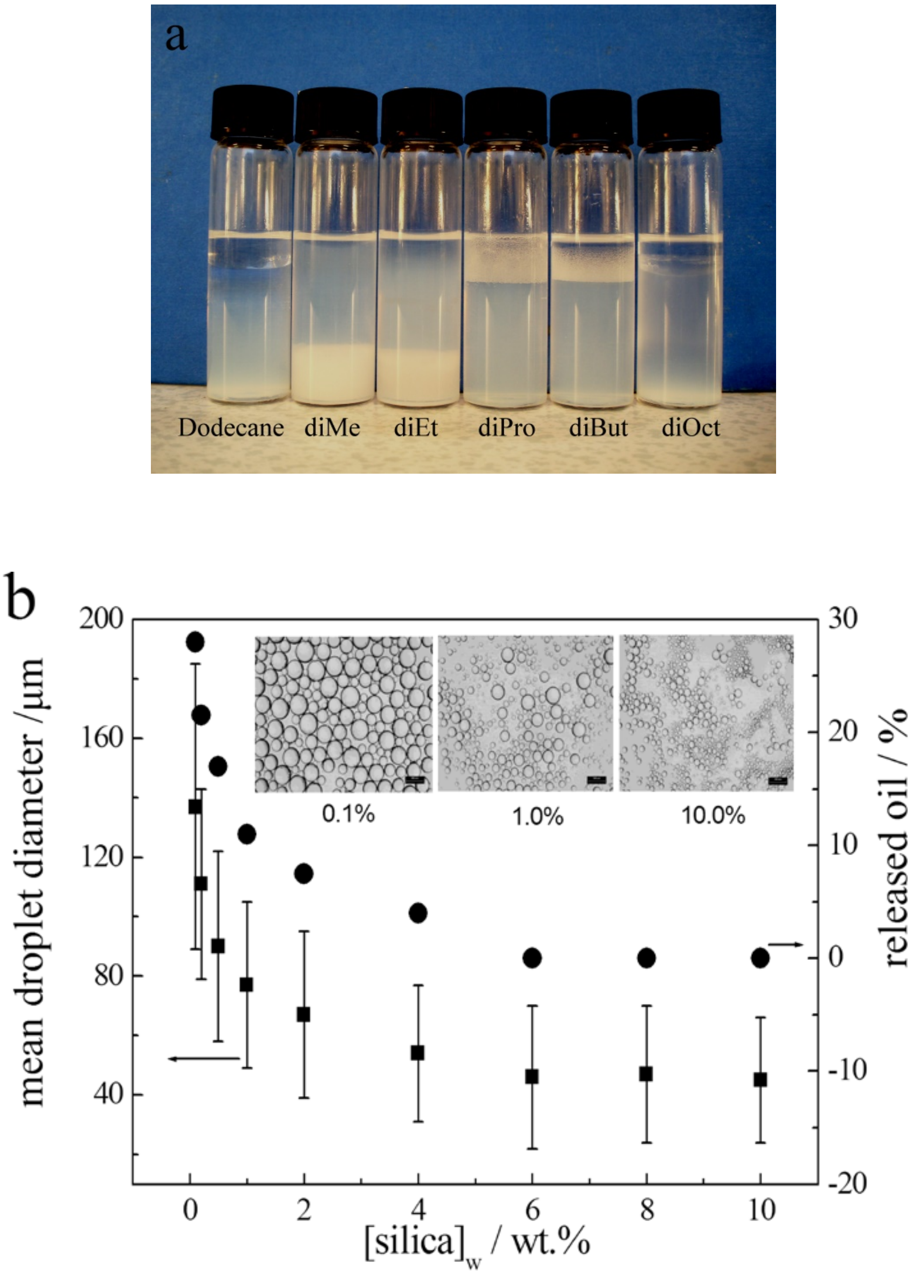

Figure 2. (a) Postulated mechanism of modification of particle surfaces by oil enabling emulsion stabilization, (b) influence of solubility of adipate in water on the coalescence of o/w emulsions of adipate oil at two time intervals (ϕ_o = 0.2, 1 wt.% N20 silica).

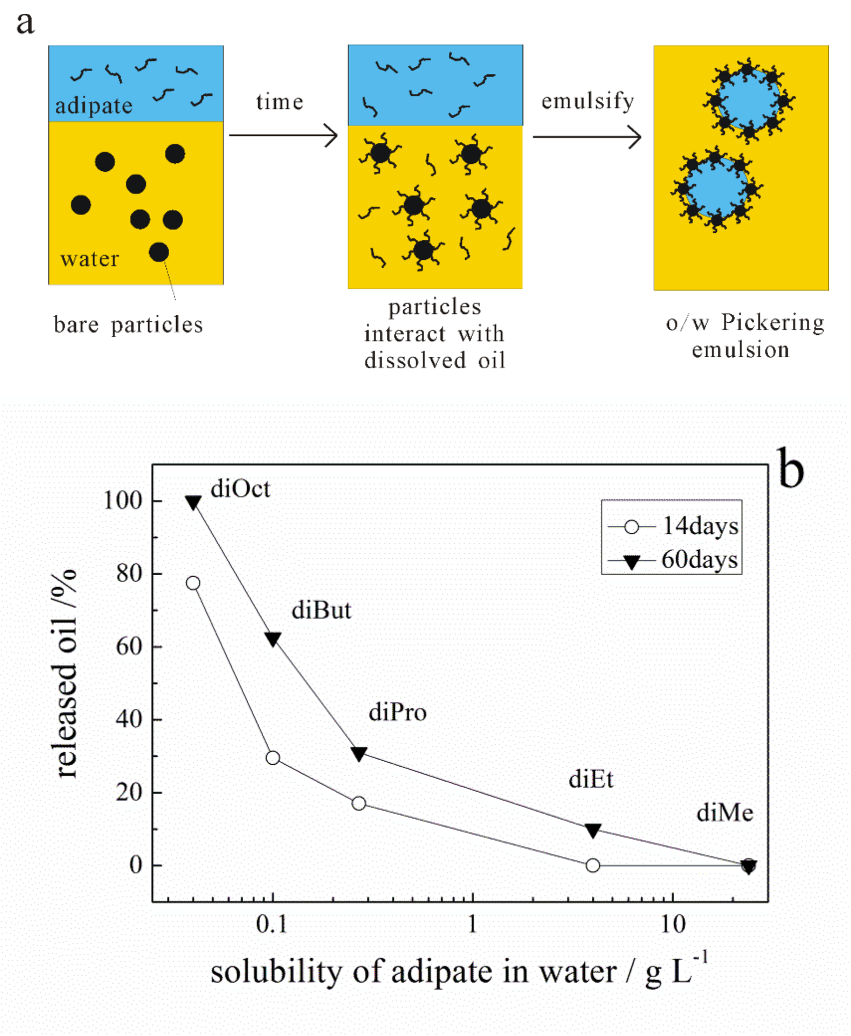

Figure 3. (a) Variation of the contact angle through water at the hydrophilic glass-dialkyl adipate-water interface *versus* the number of C atoms in the oil; oil and water were mutually saturated before measurement, (b) percentage of oil released after 2 months from adipate oil-in-water emulsions *versus* the above contact angle (ϕ_o = 0.2, 1 wt.% N20 silica).

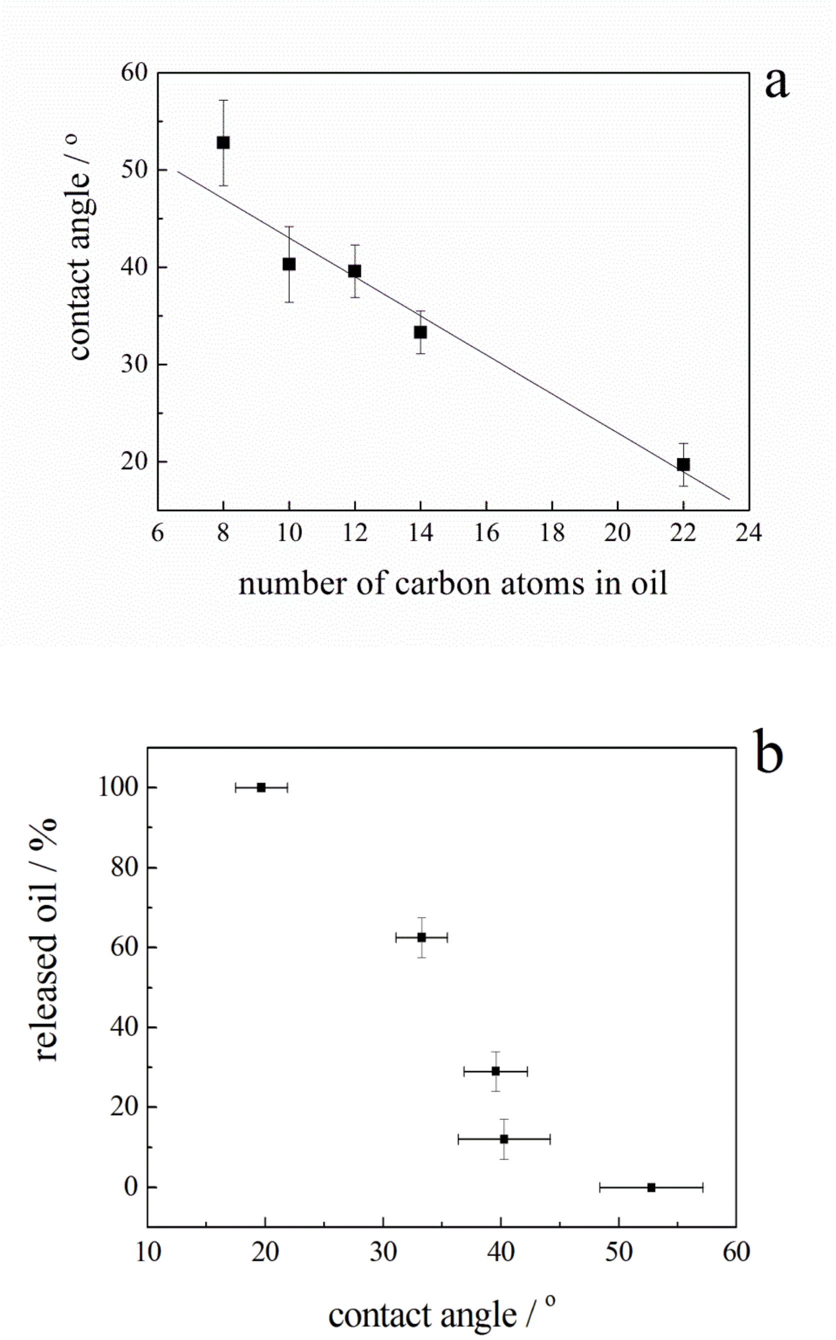

Figure 4. (a, c) Photos of dodecane-in-water emulsions after preparation (ϕ_o = 0.2, 1 wt.% N20 silica) and (b, d) percentage of oil released at different times *versus* concentration of dialkyl adipate in water for (a, b) diMe and (c, d) diEt. Average oil droplet diameter after 2 weeks is also shown in (b).

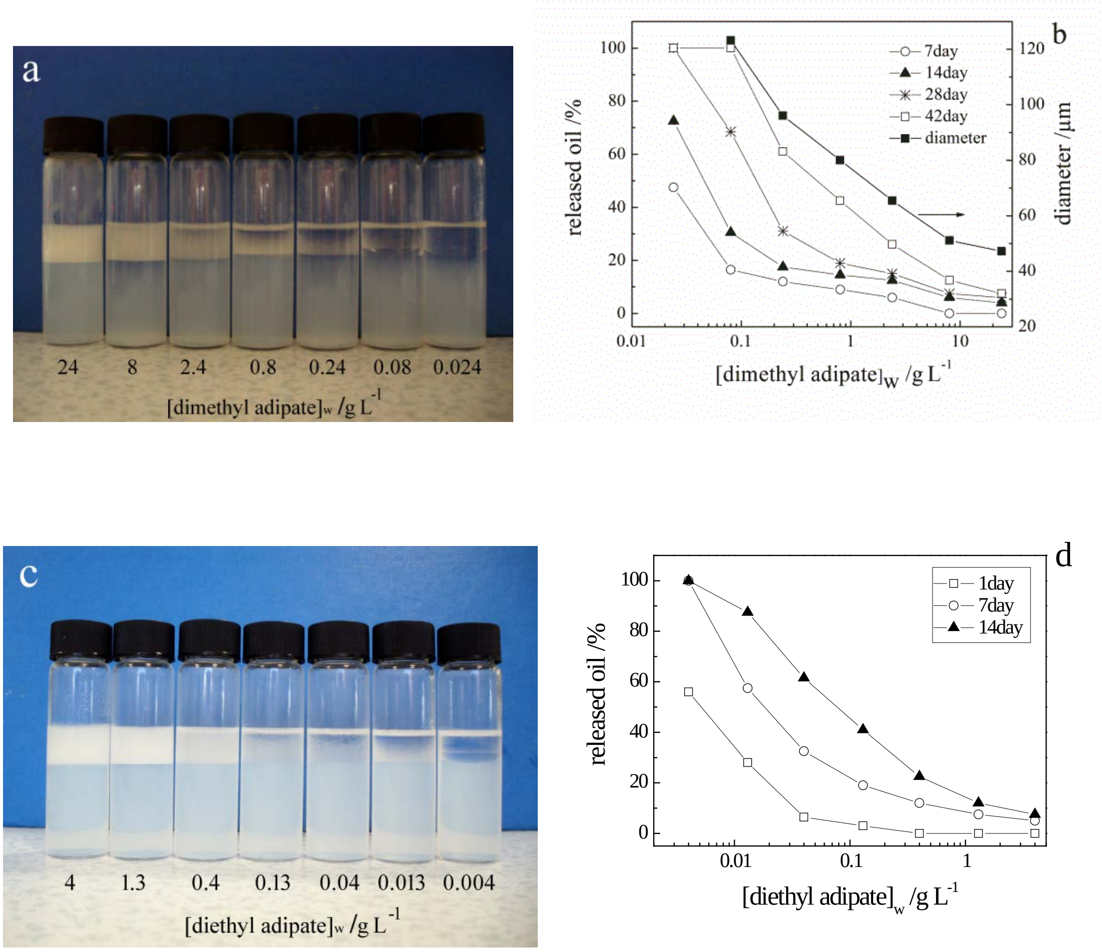

Figure 5. Variation of (a) air-water surface tension, (b) zeta potential of N20 silica particles dispersed in aqueous dimethyl adipate and (c) contact angle through water at the hydrophilic glass-dodecane-aqueous dimethyl adipate interface *versus* concentration of dimethyl adipate in water.

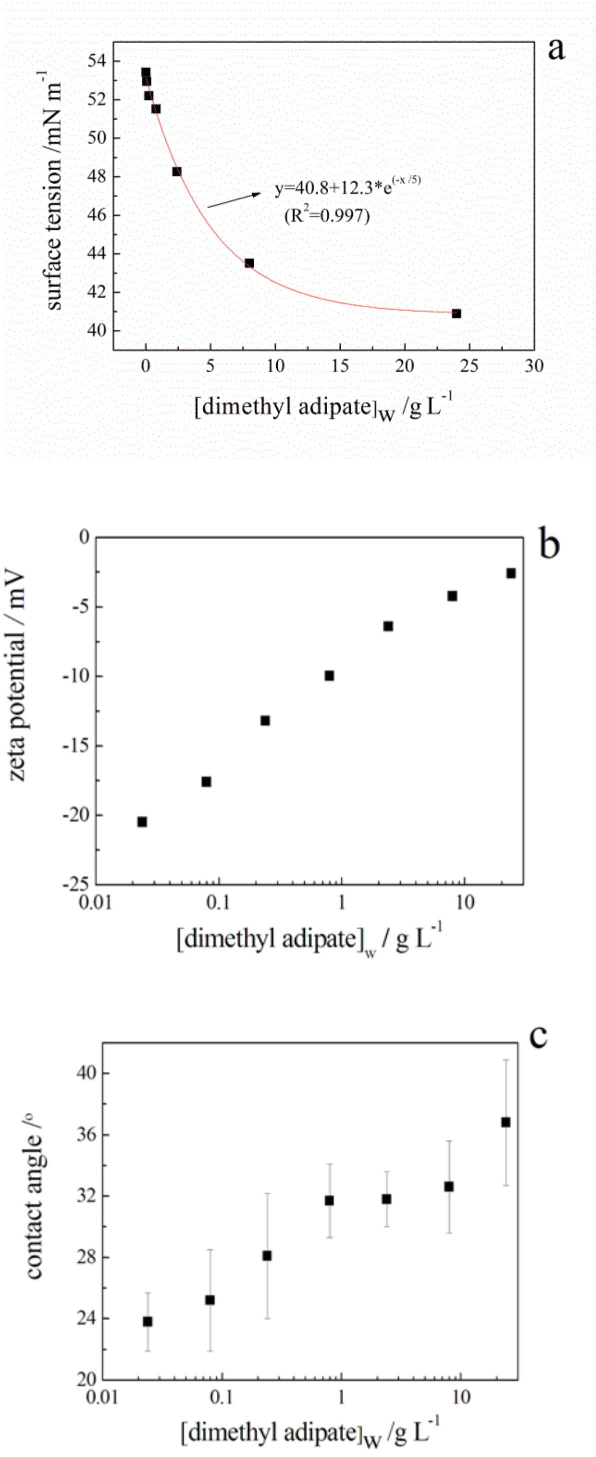

Figure 6. (a) Photos of vessels containing dodecane, ϕ_o = 0.2, and the separated aqueous phase from an adipate-in-water emulsion (1 wt.% N20 silica in water) for different adipates two weeks after emulsification, (b) variation of extent of coalesced dodecane at different times from emulsions in (a) with solubility of adipate in water.

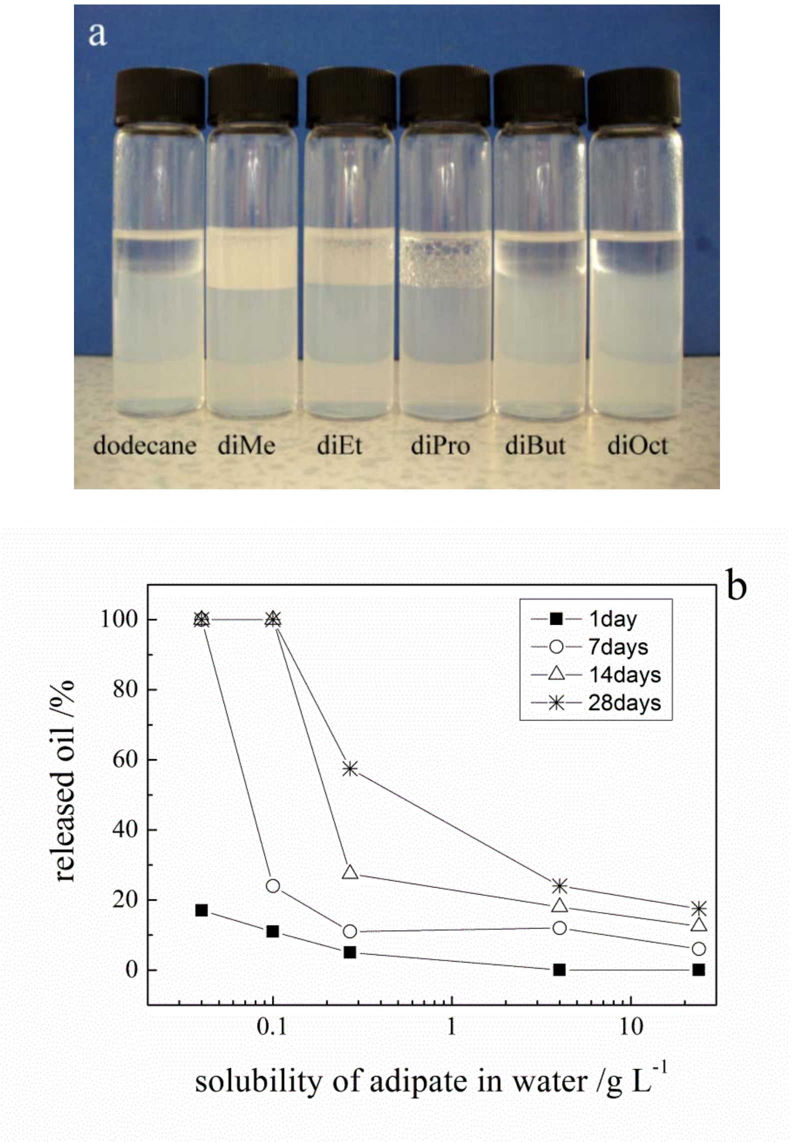

Figure 7. (a) Appearance of dodecane-in-water emulsions one month after preparation (ϕ_o = 0.2, 1 wt.% N20 silica in water) in which water is saturated by different dialkyl adipates (given), (b) variation of coalesced dodecane with solubility of adipate in water.

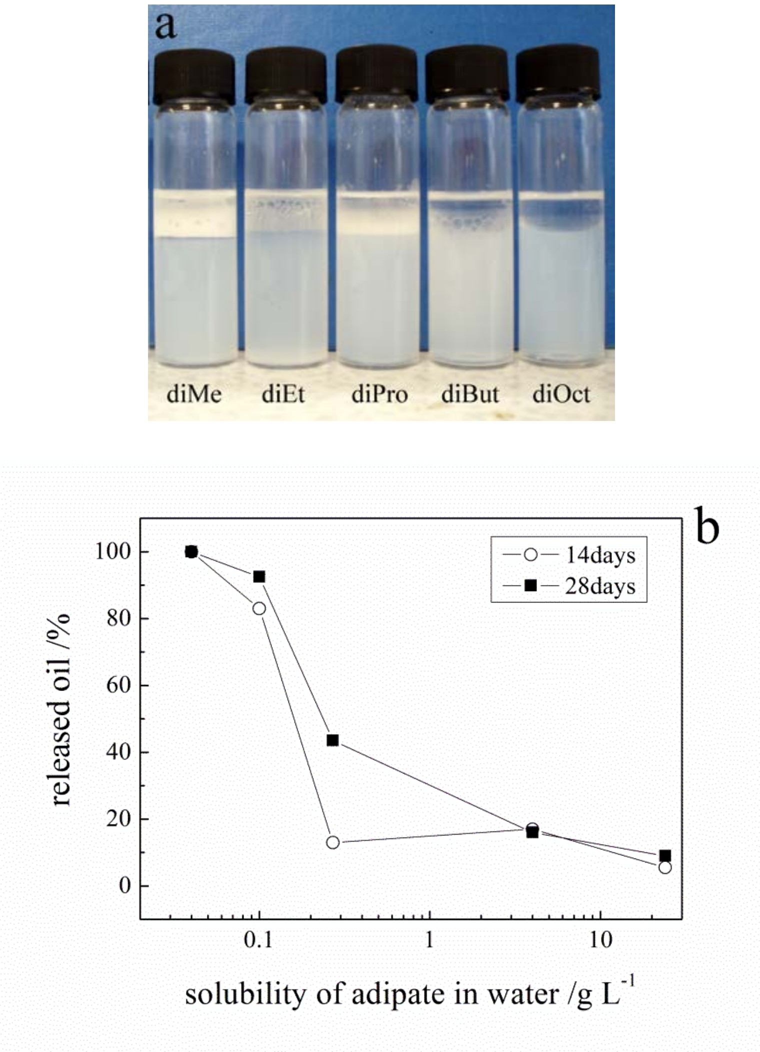

Figure 8. FT-IR spectra and calculated values of A_{1732}/A_{473} from N20 silica particles in (a) water and (b-f) drained water from o/w emulsions of (b) diOct, (c) diBut, (d) diPro, (e) diEt and (f) diMe.

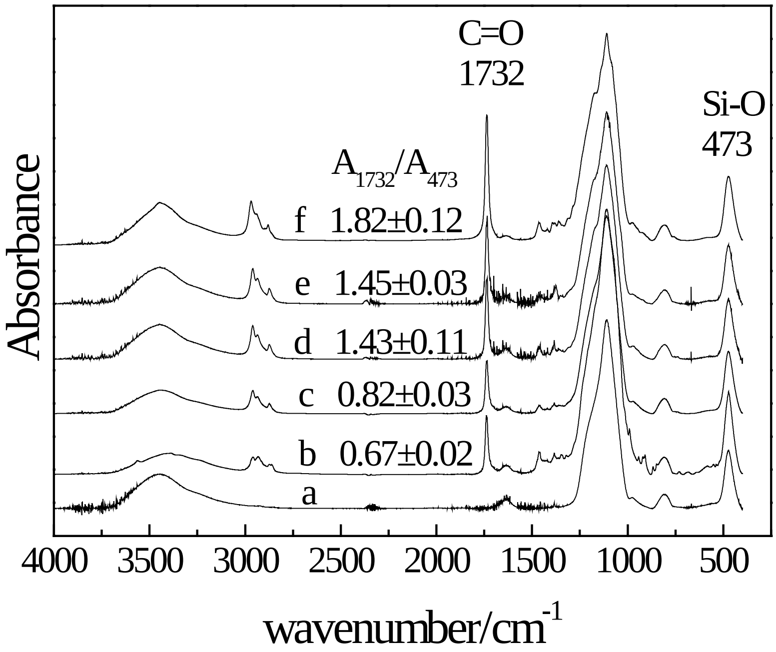

Figure 9. Extent of oil released from dipropyl adipate-in-water emulsion (ϕ_o = 0.2) stabilized by 1 wt.% of N20 silica particles dispersed in water of different pH at different times. Inset shows ionization of surface silanol groups with pH increase.

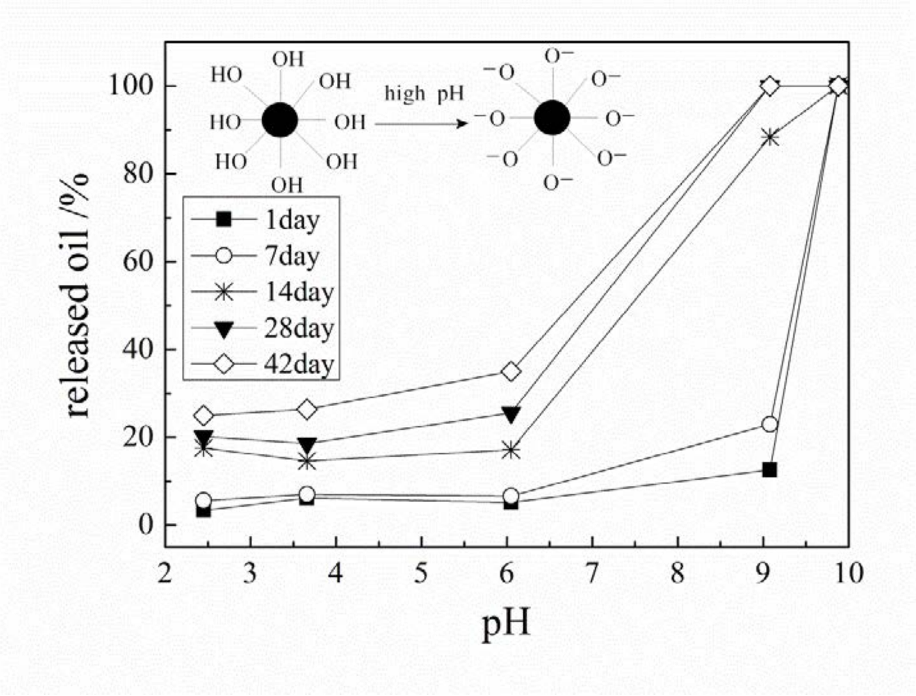

Figure 10. Appearance of dodecane- or adipate oil-in-water emulsions 2 weeks after preparation (ϕ_o = 0.2, 1 wt.% particles in water) stabilized by (a) ZrO_2 nanoparticles at pH = 1.7 and (b) Ludox HS30 nanoparticles at pH = 9.8. (c) Variation of extent of coalesced oil with the number of C atoms in the adipate oil for the three hydrophilic particle types.