

Thermo-Responsive Pickering Emulsions Stabilized by Silica Nanoparticles in Combination with Alkyl Polyoxyethylene Ether Nonionic Surfactant

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Abstract

We put forward a simple protocol to prepare thermo-responsive Pickering emulsions. Using hydrophilic silica nanoparticles in combination with a low concentration of alkyl polyoxyethylene monododecyl ether ($C_{12}E_n$) nonionic surfactant as emulsifier, oil-in-water (o/w) emulsions can be obtained which are stable at room temperature but demulsified at elevated temperature. The stabilization can be restored once the separated mixture is cooled and re-homogenized, and this stabilization-destabilization behavior can be cycled many times. It is found that the adsorption of nonionic surfactant at the silica nanoparticle-water interface *via* hydrogen bonding between the oxygen atoms in the polyoxyethylene headgroup and the SiOH groups on particle surfaces at low temperature is responsible for the *in situ* hydrophobization of the particles rendering them surface-active. De-hydrophobization can be achieved at elevated temperature due to weakening or loss of this hydrogen bonding. The time required for demulsification decreases with increasing temperature and the temperature interval between stabilization and destabilization of the emulsions is affected by the surfactant headgroup length. Experimental evidence including microscopy, adsorption isotherms and three-phase contact angles is provided to support the mechanism.

Introduction

It is well known that conventional emulsions stabilized by surfactants or polymers^[1] are thermodynamically unstable and may not be suitable for long time storage. Those stabilized by surface-active colloid particles however, known as Pickering emulsions, may be kinetically stable due to irreversible adsorption of the colloid particles at the oil-water interface which provides a physical barrier to the coalescence of droplets^[2-4]. On the other hand, however, demulsification of Pickering emulsions is relatively difficult^[5]. This is necessary in some technical or industrial applications of emulsions, especially when temporary stabilization of emulsions is required such as in polymerization, transport of oil products and fossil fuel production.^[6] Stimuli-responsive Pickering emulsions which can be transformed between stable and unstable by certain triggers are therefore of interest and attention has been paid to them in recent years^[6, 7].

The key to prepare a stimulus-responsive Pickering emulsion is to develop colloid particles which can be transformed between surface-active and surface-inactive in response to a given stimulus^[6, 7]. Much progress has been made in recent years in this context as reviewed by Tang *et al.*^[7], where individual triggers including pH,^[8-13] temperature,^[14-20] redox,^[21] light irradiation,^[22, 23] CO₂/N₂ addition,^[24-28] magnetic field^[29, 30] and dual triggers such as pH-temperature,^[31-34] light-temperature^[35] and magnetic field intensity-temperature^[36, 37] have been reported. Among these triggers both light irradiation and CO₂/N₂ triggers are environmentally benign, but the efficiency of demulsification *via* light irradiation is easily affected by the turbidity of the emulsion^[6, 7], and the CO₂/N₂ trigger involves both complicated particle synthesis and rigorous conditions such as temperatures far below or far beyond room temperature^[6]. The pH trigger is very convenient in operation. However, the addition of acids and bases and the resulting neutralization products contaminate the systems. A similar drawback is suffered by a redox

trigger. On the other hand the temperature trigger, which avoids the addition of chemicals and is easily achievable, is still attractive when the energy cost is not a problem.

Until now, the temperature- or thermo-triggered colloid particles for preparing stimuli-responsive Pickering emulsions are mostly polymeric particles, [14-16, 31, 32, 38] hybrid particles where an organic [17-19, 33, 34, 39] or inorganic [20, 36, 40, 41] core was grafted with functional polymers as well as natural biopolymer particles.^[42] However, the synthesis of these particles is complicated and some of the methods are not suitable for commercial production of large amounts. It has been reported that charged inorganic nanoparticles which are originally surface-inactive at an oil-water interface can be hydrophobized *in situ* to become surface-active [43-45] by adsorbing oppositely charged surfactant in water. When a switchable surfactant is used, the trigger of the surfactant can be transferred to particles to give switchable surface-active nanoparticles, [6] which can be employed for preparing stimuli-responsive Pickering emulsions and foams [6, 46]. Here the hydrophilic particles adsorb oppositely charged surfactant *via* electrostatic interaction with the surfactant forming a monolayer at the particle-water interface with its hydrophobic tail towards water thus enhancing the hydrophobicity of the particles. Once the electrostatic interaction is removed, *e.g.* by transforming a switchable surfactant from its charged form to its uncharged form [6] or by formation of an ion pair between conventional ionic surfactants [47], the *in situ* hydrophobization can be reversed. In this protocol, the surfactant concentration required is very low, usually $\leq 10\%$ of the critical micelle concentration (cmc), which is economically beneficial for practical applications. In this paper, we report a protocol for obtaining thermo-responsive silica nanoparticles used to prepare thermo-responsive Pickering oil-in-water emulsions, where a nonionic surfactant is chosen to replace the cationic one. We find that at low temperature the nonionic surfactant adsorbs at the silica particle-water interface with

head-on configuration *via* hydrogen-bonding between the oxygen atoms in the polyoxyethylene (POE) headgroup and the SiOH groups on particle surfaces to render particles surface-active. At elevated temperature, the hydrogen-bonding is weakened sufficiently reverting the silica nanoparticles to their original bare and surface-inactive state inducing demulsification. The effect of the POE length is examined and microscopy, adsorption and relevant contact angle data are provided for elucidating the mechanism involved.

Experimental

Materials

Silica nanoparticles (HL-200, 99.8%) with a primary particle diameter of 20 nm and a BET surface area of 200 ± 20 m²/g were provided by Wuxi Jinding Longhua Chemical Co., China. A SEM image and a TEM image of the particles are shown in Figure S1. Tetraethylene glycol monododecyl ether (C₁₂E₄, > 98%), pentaethylene glycol monododecyl ether (C₁₂E₅, > 98%) and decaethylene glycol monododecyl ether (C₁₂E₁₀, > 98%) were purchased from Sigma and used as received. Diethylene glycol monododecyl ether (C₁₂E₂, > 97%) and triethylene glycol monododecyl ether (C₁₂E₃, > 97%) were synthesized in-house^[48] using bromododecane (AR, 98%) *via* the Williamson reaction with diethylene glycol and triethylene glycol (AR grade) respectively. The ¹HNMR spectra of the two surfactants are shown in Figure S2. Dodecane (> 98%) and toluene (99.5%) were purchased from Aladdin and Sinopharm Chemical Reagent Co. respectively and were columned three times through neutral alumina before use. All other chemicals were analytically pure and purchased from Sinopharm Chemical Reagent Co. Ultrapure water with a resistance of 18.2 MΩ cm and a pH of 6.1 at 25 °C was produced from a Simplicity Pure Water System (Merck Millipore, Shanghai). All chemicals were used as received

unless specified otherwise.

Preparation and characterization of emulsions

Silica powder was weighed into a glass vessel of dimensions 6.5 cm (h) by 2.5 cm (d) (25 mL) followed by adding pure water or an aqueous solution of a nonionic surfactant. The particles were then dispersed using an ultrasound probe (JYD-650, Shanghai) of tip diameter 0.6 cm operating at an output of 50 W for 1 min. Then, an equal volume (7 mL) of aqueous phase containing either nonionic surfactant or silica nanoparticles or both and oil phase (toluene or dodecane) were placed in a glass vessel (25 mL) followed by homogenization at 11,000 rpm for 2 min using an ultra-turrax homogenizer (IKA T18 basic, S18N-10G head) at room temperature (22 ± 2 °C). The concentrations of particle and surfactant are expressed as weight percentage (wt.%) relative to the aqueous phase and moles per litre relative to the aqueous or oil phase, respectively. The emulsion type was identified using the drop test,^[44] and emulsion stability was evaluated from photographs. Micrographs of both fresh and dried emulsions at different times were recorded using a VHX-1000 microscope system (Keyence Co.).

Demulsification/emulsification cycling of emulsions

Stable emulsions containing 0.5 wt.% silica nanoparticles in combination with a low concentration of nonionic surfactant were demulsified by heating with gentle magnetic stirring (*ca.* 100 rpm) in a water bath at constant temperature until complete separation of the oil and aqueous phases occurred. Then the separated oil-water mixture was cooled down to room temperature and was re-homogenized at 11,000 rpm for 2 min. This process was repeated several times as required.

Measurements

(a) Surface tension

The air-water surface tension of aqueous solutions of nonionic surfactant with and without silica nanoparticles was measured by the du Noüy ring method at 25 ± 0.5 °C using a home-built instrument [44].

(b) Adsorption of nonionic surfactant at particle-water interface

The adsorption isotherm of C₁₂E₅ at the silica particle-water interface from aqueous solution was measured by depletion at 25 °C. Here, 0.5 wt.% silica nanoparticles were dispersed in aqueous solutions of C₁₂E₅ of different concentration using ultrasound and the dispersions were allowed to stand for 24 h at 25 °C to reach adsorption equilibrium at the solid-water interface (no sedimentation of particles was observed). Then the dispersion was transferred to a measuring vessel for surface tension measurement (without separating the particles). The equilibrium concentrations (< cmc) of C₁₂E₅ in the dispersions were obtained from the measured surface tension by calibration with the surface tension of C₁₂E₅ solutions without silica particles. [49]

(c) Contact angle at oil-water-quartz and air-water-quartz interface

Quartz slides (Beijing Zhongjingkeyi Technology Co. Ltd.) were cut into strips of 1.5 cm width and soaked in a 30% aqueous NaOH solution for 24 h, followed by rinsing using pure water and drying in air. A clean strip was placed in a cubic cuvette (35mm (L) × 25mm (D) × 20mm (H)) with the two ends being supported by two standing legs. The cuvette was filled with an aqueous solution of C₁₂E₅ until the strip was immersed. After reaching adsorption equilibrium (24 h), a toluene drop of 1 μL was released from a U-shaped needle underneath the strip in solution, which was captured by the strip to form an inverted sessile drop. The contact angle through the aqueous phase was measured using a Dropmeter A-100 drop shape analyzer (Ningbo

Haishu Maishi Scientific Test Co.). To measure the contact angle at the air-water-quartz interface, a 1 μL drop of aqueous C_{12}E_5 solution was released from a needle to a clean quartz slide to form a sessile drop. The temperature was kept at 25 ± 0.5 $^\circ\text{C}$ during measurement using an air-therm heater (Air-Thermz-ATX, World Precision Instruments).

(d) Partition coefficient of nonionic surfactants between toluene and water

5 mL toluene and 5 mL pure water with nonionic surfactant dissolved in either toluene or water at a certain concentration were mixed thoroughly in a glass vessel followed by further pre-equilibrating for more than 12 h at 25 $^\circ\text{C}$ and 45 $^\circ\text{C}/60$ $^\circ\text{C}$ using a perpendicular rotator. After a further 12 h without stirring, the toluene layer was then separated and the concentration of surfactant was measured using an HPLC instrument (Ultimate 3000 RS, Thermo Fisher Scientific) equipped with an evaporation-light scattering detector (ELSD 6000, Alltech) and a column of Hadera ODS-2 4.6 mm \times 250 mm filled with silica particles of 10 nm – 5 μm . The instrument was operated at a N_2 pressure of 25 psi and a detection temperature of 60 $^\circ\text{C}$ using methanol as flow liquid at a flow rate of 0.8 mL/min and a gas flow rate of 1.6 mL/min. The surfactant concentration in toluene was calculated from the peak area using a standard area-concentration correlation obtained from solutions of known concentration of surfactant in toluene as calibration.

(e) Determination of silica nanoparticle concentration in the aqueous phase of emulsions

Toluene-in-water emulsions (10 mL/10 mL) stabilized 0.5 wt.% silica nanoparticles in combination with 0.3 mM C_{12}E_5 were prepared in a vessel of 40 mL (2.7 cm (d) \times 9.5 cm (h)) as described above. For one emulsion, the aqueous phase separated after creaming at 25 $^\circ\text{C}$ was removed using a syringe and was transferred to a glass vessel of 25 mL which had previously been dried and weighed. The mass of aqueous phase was recorded. The water in the solution was evaporated by heating close to 100 $^\circ\text{C}$ in an oven and the particles were finally dried at 110 $^\circ\text{C}$ to

constant weight. The weight of the particles remaining was obtained from which the concentration (mass percentage) of silica nanoparticles dispersed in the aqueous phase of the emulsion can be calculated. The remainder of the particles is considered adsorbed at droplet interfaces in the emulsion. For other emulsions, a similar procedure was followed after demulsification at 45 °C.

(f) Phase inversion temperature of dodecane-water emulsion stabilized by C₁₂E₅

The phase inversion temperature (PIT) of dodecane-water emulsions stabilized solely by C₁₂E₅ was measured using conductivity. The aqueous solution contained 6 mM C₁₂E₅ and 1.0 mM NaCl. 7 mL aqueous solution and 7 mL dodecane were added to a glass vessel (25 mL), which was placed in a thermostatic water bath with temperature being controlled at a precision of 0.1 °C. When the specified temperature was achieved, the mixture was homogenized within the water bath as described above to form an emulsion, whose conductivity was measured immediately using a digital conductivity meter (FE30, Mettler Toledo). A series of batch emulsions was prepared at different temperatures between 35 °C and 45 °C. The conductivity of emulsions stabilized by silica nanoparticles in combination with C₁₂E₅ was similarly measured over a wider temperature range, in which the aqueous phase contained 0.5 wt.% of particles, 6 mM C₁₂E₅ and 1.0 mM NaCl.

Results and discussion

(a) Formation of Pickering emulsions at room temperature

The hydrophilic silica nanoparticles (HL-200) are negatively charged at pH > 3, as shown in Figure S1(c). The nonionic surfactant C₁₂E₅ dissolves in pure water giving a transparent solution at room temperature (22 °C) in accordance with its hydrophilie-lipophile balance number of 11.7,

and a 1 wt.% solution exhibits a cloud point of 31 °C. The air-water surface tension against surfactant concentration (C) curve at 25 °C is shown in Figure 1, yielding a cmc of 0.06 mM in good agreement with the literature value of 0.07 mM ^[50]. The calculated saturation adsorption (Γ^∞) near the cmc is equal to 3.5×10^{-10} mol/cm² corresponding to an area per molecule of 0.47 ± 0.03 nm².

The bare silica nanoparticles alone at a concentration of 0.5 wt.% cannot stabilize a toluene-in-water emulsion at room temperature due to their extreme hydrophilicity, ^[6] as shown in Figure 2(A) where very large droplets and coalesced oil phase were observed in the upper layer. For C₁₂E₅ alone, although it prefers to stabilize toluene-in-water emulsions, ^[51] they are extremely unstable and no stable emulsion can be formed at initial concentrations in water below 1 mM as shown in Figure 2(B). Based on HPLC measurements, a partition coefficient $P = C_o/C_w = 3.17$ for C₁₂E₅ between toluene and water at 25 °C was measured for an initial concentration of 0.3 mM dissolved initially in either water or toluene, as shown in Table 1 and Figure S3, indicating that 3/4 of the surfactant distributes as monomer in favour of the toluene phase. Thus concentrations much higher than the cmc in water are needed to prepare stable emulsions. ^[52] In fact, no stable emulsion was obtained at concentrations up to 90 mM in water when toluene was used as the oil phase. However, when 0.5 wt.% silica nanoparticles were dispersed in aqueous solutions of C₁₂E₅ at low concentration (0.01-1 mM), relatively stable toluene-in-water emulsions were formed by homogenization. These emulsions showed almost no change in appearance after one week at room temperature as seen in Figures 2(C) and (D), and although creaming occurred no coalescence was visible up to at least 3 months. The average droplet diameter decreases with increasing surfactant concentration from *ca.* 400 μ m at 0.06 mM to 50-100 μ m at 1 mM (Figure 3). The latter is still larger than that (15-40 μ m) of a dodecane-in-water emulsion stabilized by

C₁₂E₅ alone at 3 mM as shown in Figure 3(F), indicating that these droplets are mainly stabilized by surfactant-coated particles instead of C₁₂E₅ molecules, although the latter may also adsorb at the oil-water interface. The emulsions stabilized by silica in combination with a low concentration of C₁₂E₅ are therefore Pickering emulsions.

(b) Thermo-responsive character of Pickering emulsions

Although the Pickering emulsions containing particles and surfactant remained stable to coalescence at room temperature for more than 3 months, demulsification occurred once the emulsions containing 0.5 wt.% silica and C₁₂E₅ at different concentrations were placed in a water bath at 45 °C and subjected to gentle magnetic stirring. As an example, the demulsification process at 45 °C is shown in Figure S4, where demulsification was observed as a gradual process under gentle stirring (*ca.* 100 rpm) and complete phase separation occurred after about 35 min, whereas no demulsification was observed up to 2 h without stirring. Stirring is therefore necessary for demulsification, which may increase the contact opportunity of oil droplets in the aqueous phase and enhance diffusion of the nonionic surfactant from the aqueous phase to the oil phase at elevated temperature, accelerating desorption of nonionic surfactant from particle surfaces and thereby desorption of particles from oil-water interfaces. It was also noticed that demulsification is accelerated upon increasing the stirring speed. A stirring speed of *ca.* 100 rpm was thus selected to evaluate the effects of temperature and surfactant concentration on demulsification.

The time required to achieve complete phase separation at 45 °C increases with increasing C₁₂E₅ concentration, from *ca.* 10 min for 0.03 mM C₁₂E₅ to *ca.* 45 min for 1 mM C₁₂E₅ (it takes about 4 min for the temperature of the emulsion to increase from 22 °C to 45 °C), Figure 4(a).

Alternatively, at a lower temperature of 30 °C, it takes longer (120 min for 0.3 mM C₁₂E₅) to achieve complete phase separation. Once the temperature is increased to 35 °C and beyond the time required decreases almost linearly with increasing temperature, as shown in Figure 4(b). Then, once the separated oil-water mixture was cooled down to room temperature, a stable Pickering emulsion was formed again by re-homogenization. Although homogenization at 45 °C yielded a temporary stable emulsion, it demulsified quickly (19 min) at 45 °C with gentle stirring whereas the emulsion homogenized at 25 °C remained stable. This demulsification/emulsification pattern was cycled six times as shown in Figure 5(A), and the micrographs shown in Figure 6 indicate that the average emulsion droplet size decreases slightly after each cycle. This may be caused by a decrease of the oil-water interfacial tension following successive emulsification/demulsification cycles. Prior to the first homogenization, the surfactant is dissolved in the aqueous phase and the interfacial tension is 7.1 ± 0.6 mN/m; monomer partitioning to oil is not fully achieved however. After two cycles of emulsification/demulsification, the interfacial tension decreases to 5.6 ± 0.1 mN/m following achievement of surfactant partitioning and equilibrium adsorption.

Similar demulsification/emulsification cycling can be achieved when using dodecane as the oil phase, as shown in Figure 5(B). The reduced monomer solubility of C₁₂E₅ in dodecane compared with toluene leads to the formation of stable dodecane-in-water emulsions using C₁₂E₅ as emulsifier alone, as shown in Figure 3 (F). An o/w emulsion stabilized by C₁₂E₅ alone at 6 mM can be phase inverted to water-in-oil by heating with a phase inversion temperature of around 41 °C being determined from emulsion conductivity measurements (Figure S5). In the presence of 0.5 wt.% silica nanoparticles, however, no phase inversion is observed up to 75 °C and the emulsion conductivity remains almost constant and high indicative of o/w emulsions.

Nevertheless, the time required for complete phase separation of the dodecane-in-water emulsion at 45 °C is similar to that for the toluene-in-water emulsion (35 min).

(c) Effect of POE chain length

To examine the effect of the POE chain length on the formation of Pickering emulsions and their thermo-responsive character, a series of pure nonionic surfactants with either shorter or longer POE chain length than 5 ($C_{12}E_m$, $m = 2, 3, 4$ and 10) was investigated. Since the shorter analogues with $m = 2, 3$ or 4 are less soluble in water, they were initially dissolved in toluene. Partitioning of monomeric surfactant into water occurs to a greater or lesser extent depending on the value of m (Table 1). The results for $C_{12}E_4$ and $C_{12}E_{10}$ are shown in Figures 7 and 8 respectively, and those with $C_{12}E_3$ and $C_{12}E_2$ are shown in Figures S6 and S7, respectively.

It is seen that at room temperature although the nonionic surfactants with relatively short POE chains ($m = 2, 3$ or 4) favor toluene-in-water emulsions at high concentration (100 mM), the emulsions are not stable at concentrations ≤ 10 mM. However, mixtures of 0.5 wt.% silica nanoparticles in combination with these surfactants at low concentration do stabilize Pickering toluene-in-water emulsions. A distinct character for these systems is that the minimum concentration of the nonionic surfactant required to prepare a stable Pickering emulsion increases upon decreasing the POE chain length. It is approx. 0.01 mM for $C_{12}E_5$ (initially in water), 0.3 mM for $C_{12}E_4$, 3 mM for $C_{12}E_3$ and 10 mM for $C_{12}E_2$ (initially in toluene). This is probably due to an increase in the partitioning of monomeric surfactant to the oil phase upon decreasing the POE chain length (Table 1), leaving a lower concentration in water where particles originate. However, all these toluene-in-water Pickering emulsions can be demulsified upon increasing the temperature. This holds for all surfactant concentrations. For example, at 45 °C complete phase

separation occurs in about 30 min for emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with either 6 mM C₁₂E₄ or 10 mM C₁₂E₂, and the cooled mixtures re-form stable emulsions upon re-homogenization. The demulsification/emulsification cycling for the two emulsions is shown in Figure 7 and Figure S7, respectively.

By contrast, the nonionic surfactant C₁₂E₁₀ is very soluble in water (cloud point of 1 wt.% solution = 79 °C) and can form toluene-in-water emulsions alone stable to coalescence once the concentration in water reaches around 1 mM (cmc = 0.04 mM at 25°C, Figure S8), as shown in Figure 8(A). This is because partitioning of its monomer to oil is significantly reduced as a result of the very hydrophilic headgroup (Table 1). When 0.5 wt.% silica nanoparticles were dispersed in this nonionic surfactant solution, stable toluene-in-water Pickering emulsions were now formed at concentrations of C₁₂E₁₀ as low as 0.06 mM or 1.5 cmc seen in Figure 8(B). Their average droplet diameters decrease with increasing surfactant concentration (Figure 8, a-d), similar to that for C₁₂E₅ emulsions. The minimum concentration of C₁₂E₁₀ required to form a stable emulsion (0.06 mM) is higher than that for C₁₂E₅ (0.01 mM) however. This may be caused by the long headgroup length in C₁₂E₁₀ which reduces the tendency of the surfactant to adsorb at particle surfaces and leads to reduced hydrophobisation *in situ*. For a Pickering emulsion stabilized by 0.5 wt.% silica and 0.1 mM C₁₂E₁₀, complete demulsification/phase separation was not observed at 45 °C with gentle stirring for up to 4 h and no significant increase in droplet size was noticed, Figure 8 (b and b'). However, partial phase separation was achieved at 60 °C with stirring for more than 1 h and complete phase separation was achieved at 79 °C with stirring for 20 min (Figure 8(C)). A stable Pickering emulsion was then re-formed by homogenization after cooling the separated oil-water mixture to 25 °C. At a lower C₁₂E₁₀ concentration of 0.06 mM, the emulsion formed at 25 °C is less stable initially and easily demulsified within 10 min at 79 °C,

suggesting that longer time may be needed at higher surfactant concentration. At higher concentrations of C₁₂E₁₀ (≥ 1 mM), the emulsion may no longer be a true Pickering emulsion since the nonionic surfactant alone also stabilizes an emulsion. This is evidenced by the micrographs shown in Figure 8 (d and e) where the size of the droplets stabilized by 0.5 wt.% silica with 1 mM C₁₂E₁₀ are similar to those stabilized by C₁₂E₁₀ alone. Also, the separated aqueous phase following creaming is cloudy suggesting the presence of non-adsorbed particles.

(d) Postulated mechanism of stabilization/destabilisation of emulsions

The experimental results above show a definite synergism between the hydrophilic silica nanoparticles and nonionic surfactant at low concentration in significantly enhancing emulsion stability. This synergism has been observed previously by other researchers [49, 53-55]. Since both the silica nanoparticles and nonionic surfactant at low concentration cannot stabilize emulsions when used alone and Pickering emulsions were formed by using their mixture, it is suggested that the hydrophilic nanoparticles are hydrophobized *in situ* by the nonionic surfactant. This occurs by the adsorption of surfactant at the particle-water interface which renders the particles surface-active. In similar mixtures, the adsorption of the coated particles at the oil-water interface of droplets has been confirmed by freeze-fracture electron microscopy [53]. Here, the adsorption of the coated-particles can be observed from micrographs of the toluene-in-water Pickering emulsion stabilized by 0.5 wt.% silica nanoparticles and 0.3 mM C₁₂E₅ shown in Figure 9. In (a), the surface of a partially dried droplet can be seen to be textured and a completely dried droplet in (b) shows cracks in the shell. This is supported by the data shown in Table 2 where in the Pickering emulsion around 38% of the silica nanoparticles adsorbed at droplet surfaces after emulsification at 25°C. The adsorption of particles at droplet surface is also evident in mixtures

with C₁₂E₄ (c) or C₁₂E₁₀ (d). By contrast, neither of these features was observed for droplets stabilized by C₁₂E₁₀ alone at 1 mM (e and f).

When nonionic surfactant dissolves in water, hydrogen-bonding occurs between the oxygen atoms in the POE headgroup and the hydrogen atoms in water molecules. Due to the high propensity of SiOH groups on the surface of hydrophilic silica nanoparticles in water, it is believed that a nonionic surfactant adsorbs to particle surfaces *via* hydrogen-bonding involving the POE headgroup exposing the alkyl chain towards water. [48, 56, 57] This head-on configuration is akin to that of cationic surfactants which have been shown to hydrophobize the particles *in situ*. [43, 44] We have determined the adsorption isotherm of C₁₂E₅ at the silica-water interface at 25 °C by the depletion method with the equilibrium surfactant concentration in water being determined *via* surface tension measurements. [44, 49] Figure 1 shows that at the same initial surfactant concentration, the surface tensions of aqueous C₁₂E₅ solutions containing silica particles are higher than that of solutions without particles as a result of loss of some surfactant to particle surfaces. Below the cmc, the surface tension-concentration data can be well fitted by the Szyszkowski equation [1] (dashed line in Figure 1), and the equilibrium concentration of C₁₂E₅ in the particle dispersion can thus be calculated from the measured surface tension. The adsorption isotherm of C₁₂E₅ at the silica-water interface is also shown in Figure 1, with maximum adsorption (1.2 mmol/g) equivalent to 0.28 nm² per molecule being achieved at an equilibrium concentration of 0.048 mM (0.8 cmc), suggesting double layer or hemi-micelle adsorption. But at an initial concentration equal to the cmc (C_{eq} = 0.02 mM), the adsorption (7.9×10⁻³ mmol/g) is equivalent to a molecular area of 42.2 nm² per molecule suggesting sub-monolayer adsorption. This molecular area is larger than that of the cationic surfactant cetyltrimethylammonium bromide at an equivalent concentration [47], implying that the POE headgroup occupies more

adsorption sites on these particles. The maximum adsorbed amount of C₁₂E₅ (1.2 mmol/g) is larger than that of C₁₂E₇ (0.5 mmol/g) on hydrophilic fumed silica of similar surface area (200 m²/g) obtained earlier, ^[49] in agreement with the finding that nonionic surfactants with short POE headgroup usually exhibit higher adsorption than those with long POE headgroup. ^[56]

The zeta potential of the silica particles (0.1 wt.%) dispersed in aqueous C₁₂E₅ solutions at 25 °C was measured. It was found that over a wide concentration range (0.001 - 1 mM), the zeta potential remains unchanged at $- 25.6 \pm 0.3$ mV and is equal to that in pure water (- 25.2 mV). Similar results have been reported by other researchers ^[58]. This negative zeta potential along with a small primary particle size enables these silica particles to disperse well in solutions of C₁₂E₅ without sedimentation at both room temperature and beyond.

The hypothesized configuration of the nonionic surfactant at the particle-water interface with the POE headgroup towards particle surfaces is supported by measurements of the contact angle at both the air-water-quartz and the oil-water-quartz interfaces. As seen in Figure 10, the contact angle of the aqueous phase on a quartz slide in air increases with increasing C₁₂E₅ concentration, from close to 0° (pure water) to a maximum of 45° at 0.03 mM (0.5 cmc), and then decreases with further increase in surfactant concentration. This pattern of behaviour has been observed for cationic surfactants adsorbed on a negatively charged glass slide, although the maximum contact angle in the latter case is much larger. ^[44] The maximum contact angle is higher than that of nonyl phenol ethoxylated surfactants (30°) and octaethylene glycol monododecyl ether (C₁₂E₈, 25°) on hydrophilic silica surfaces obtained by Scales *et al.* using the captive bubble method. ^[59] The increase in contact angle with surfactant concentration is sufficient for the silica nanoparticles to become surface-active enabling them to stabilize emulsions. At higher concentration, it is believed that the nonionic surfactant adsorbs on silica

particle surfaces as hemi-micelles or in the form of a bilayer ^[56-57,59-61], which usually occurs at concentrations around the cmc, rendering particles hydrophilic again such that they desorb from the oil-water interface of emulsion drops. The contact angle is seen to decrease in this region. However, when air is replaced by toluene which has been pre-equilibrated with the aqueous phase containing C₁₂E₅, although the overall pattern remains unchanged, the curve moves downward and the maximum contact angle decreases to 25°. This is because a large fraction of surfactant partitions into oil (Table 1) such that the remaining concentration of C₁₂E₅ in the aqueous phase is much lower than the initial concentration. As a result, even at a high C₁₂E₅ concentration initially in water (3-30 mM), a Pickering emulsion is still formed in the presence of particles (no stable emulsion in the absence of particles) as shown in Figure S9. In contrast, when the more hydrophilic C₁₂E₁₀ was used in combination with silica, emulsions at high surfactant concentration do transform to those stabilized by surfactant alone (Figure 8(d) and (e)). This is in line with the observation that the synergism between silica particles and nonionic surfactant occurs at intermediate concentrations of surfactant. ^[49, 53, 54]

Similar to the hydrogen bonds between POE headgroups and water molecules, that between the nonionic surfactant and silanol groups on particle surfaces is thermo-sensitive, being weakened or destroyed upon increasing temperature. In emulsions stabilized solely by relatively high concentrations of nonionic surfactant, dehydration of headgroups with increasing temperature can induce emulsion phase inversion ^[1, 51]. Here, no emulsion phase inversion was observed since (a) low concentrations of surfactant are used and (b) emulsions are not stabilized by surfactant alone. On one hand destruction of the hydrogen bonds between particles and nonionic surfactant promotes desorption of surfactant from particle surfaces, and on the other hand destruction of the hydrogen bonds between nonionic surfactant and water promotes

surfactant to transfer to the oil phase, which reduces the equilibrium concentration of surfactant in the aqueous phase and thereby results in desorption of surfactant from particle surfaces. Particles are thus rendered hydrophilic and desorb from emulsion drop interfaces leading to demulsification. This is directly evidenced by the data shown in Tables 1 and 2. For the Pickering emulsion stabilized by 0.5 wt.% silica nanoparticles and 0.3 mM C₁₂E₅, the concentration of C₁₂E₅ in toluene after demulsification at 45°C was measured to be 0.275 mM, which gives an equilibrium aqueous phase concentration of 0.0145 mM based on P = 19. At this concentration, the adsorption of C₁₂E₅ at particle surfaces is as low as 3.13×10^{-3} mmol/g, equivalent to a molecular area of 106 nm², *i.e.* negligible adsorption. The silica nanoparticles are rendered hydrophilic as reflected by the percentage adsorbed at drop interfaces which decreases from 38% at 25 °C to 11% at 45 °C.

At higher temperatures, the time required for this to occur is reduced. Since the hydrogen bonding can be reversibly recovered by cooling the system to low temperature, stable Pickering emulsions are formed again at room temperature after re-homogenization. Theoretically, nonionic surfactants with smaller POE headgroups may exhibit higher adsorption^[56] at particle surfaces and thus display an increased *in situ* hydrophobization of particles. Unfortunately, the solubility of the surfactant in water decreases significantly on decreasing the number of oxyethylene groups. In the presence of toluene, monomeric nonionic surfactant of low oxyethylene number distributes heavily in favour of the oil phase (Table 1). This leads to a significant increase in the total concentration of surfactant required for the synergism to occur. However, both the time and temperature required for demulsification of the stable emulsions are similar to those required for the C₁₂E₅ system. When using a surfactant with a long POE headgroup like C₁₂E₁₀, the temperature for demulsification increases as expected. However, the efficiency of C₁₂E₁₀ in

providing synergism is lower than that of C₁₂E₅, probably due to its lower adsorption at the particle-water interface. ^[56] Nevertheless, this protocol provides a means for practical applications to obtain a suitable demulsification temperature by varying the number of oxyethylene groups in a nonionic surfactant. We believe that a good balance between high efficiency and a suitable demulsification temperature can be achieved by designing or selecting the appropriate nonionic surfactant.

Conclusions

We have demonstrated a simple protocol to prepare thermo-responsive Pickering oil-in-water emulsions by using hydrophilic silica nanoparticles in combination with a low concentration of nonionic surfactant possessing a polyoxyethylene headgroup. The Pickering emulsions are stable at room temperature but exhibit coalescence at elevated temperature and emulsification/demulsification can be cycled many times. The time required for demulsification decreases with increasing temperature but increases with increasing surfactant concentration; the demulsification temperature can also be controlled by the length of the POE headgroup. Adsorption of the nonionic surfactant at the particle-water interface *via* hydrogen-bonding is responsible for endowing the particles with sufficient surface activity for emulsion stabilization. This is lost at higher temperature leading to particle desorption from drop interfaces due to the weakening of the hydrogen bonds and increased partitioning of the nonionic surfactant to the oil phase. Those surfactants with intermediate POE headgroup length seem to be more efficient than those with either a short headgroup which distribute heavily in favour of the oil phase or those with a long headgroup which adsorb less at the particle-water interface. In general, the *in situ* hydrophobization of silica nanoparticles by nonionic surfactant is strong enough to enable

stabilization of a Pickering emulsion but is weaker than that produced by either cationic surfactant or alkyl carboxyl betaine surfactant in neutral and acidic aqueous media respectively.

Keywords: Thermo-responsive; Pickering emulsions; silica nanoparticles; nonionic surfactant; hydrophobization; contact angle

Supporting Information

SEM and TEM images of dry silica nanoparticles (HL-200) and zeta potentials of 0.1 wt.% silica nanoparticles dispersed in water of different pH, ¹HNMR spectra of C₁₂E₂ and C₁₂E₃ synthesized, peak area as a function of the concentration of nonionic surfactant in toluene *via* HPLC analysis, digital photographs of a toluene-in-water emulsion stabilized by 0.5 wt.% silica particles and 0.3 mM C₁₂E₅ held at 45 °C for different times with gentle stirring and for 120 min without stirring, conductivity of dodecane-water emulsions stabilized by 6 mM C₁₂E₅ with and without 0.5 wt.% silica nanoparticles as a function of temperature, photographs of toluene-in-water emulsions stabilized by C₁₂E₃ alone and mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₃ at different concentrations, photographs of toluene-in-water emulsions stabilized by C₁₂E₂ alone and mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₂ at different concentrations, surface tension of aqueous solutions of C₁₂E₁₀ as a function of concentration at 25 °C, photographs of toluene-in-water emulsions stabilized by C₁₂E₅ alone and mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₅ at different concentrations and micrographs of the droplets stabilized by the mixtures.

This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Table 1. Partition coefficient ($P = C_o/C_w$) of nonionic surfactant between equal volumes of toluene and water phases at different temperatures obtained by measuring C_o using HPLC. The value of C_o used to calculate P is an average of the concentration in toluene obtained with surfactant initially dissolved in either water or toluene.

Surfactant	C_w (initial) /mM	25 °C		45 °C		60 °C	
		C_o /mM	P	C_o /mM	P	C_o /mM	P
C ₁₂ E ₄	6.0	4.95 ± 0.09	4.71	5.77 ± 0.05	25.10		
C ₁₂ E ₅	0.3	0.23 ± 0.01	3.17	0.28 ± 0.01	19.00		
C ₁₂ E ₁₀	0.3	0.18 ± 0.01	1.48			0.25 ± 0.01	5.52
C ₁₂ E ₅ with 0.5 wt.% silica particles	0.3	emulsified		0.27			

Table 2. Percentage of silica nanoparticles adsorbed at oil-water interfaces in toluene-in-water emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with 0.3 mM C₁₂E₅ at two temperatures, obtained by measuring the concentration of particles remaining in the aqueous phase after emulsification, C_p .

Temperature/°C	After emulsification			% adsorbed
	V_{aq} /mL	Mass particles/g	C_p /%	
25	4.9983	0.0154	0.308	37.4 ± 1.4
25	5.0023	0.0159	0.318	
45	5.0121	0.0227	0.453	11.0 ± 2.2
45	5.0051	0.0219	0.438	

Figure 1. Surface tension (left ordinate) of aqueous $C_{12}E_5$ solutions without and with 0.5 wt.% silica nanoparticles and adsorbed amount (right ordinate) of $C_{12}E_5$ at the silica nanoparticle-water interface as a function of initial and equilibrium $C_{12}E_5$ concentration, respectively at 25 °C. Dashed line is the fit to the data for calculation of the surface concentration.

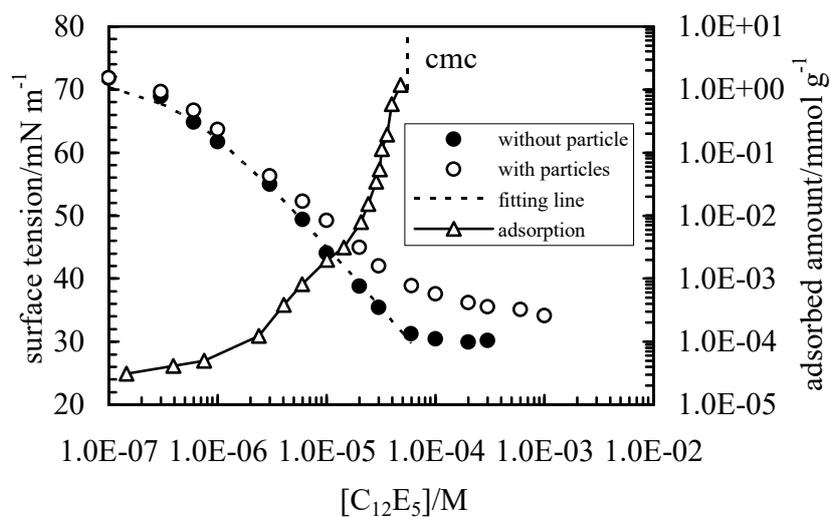


Figure 2. Photographs of vessels containing toluene-in-water (7 mL/7 mL) emulsions stabilized by (A) 0.5 wt.% silica nanoparticles alone, (B) C₁₂E₅ alone at different concentrations and (C), (D) mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₅ at different concentrations taken 24 h (A-C) and 1 week (D) after preparation. [C₁₂E₅]/mM in water from left to right: 0.01, 0.03, 0.06, 0.1, 0.3, 0.6 and 1. Temperature = 22 ± 2 °C.

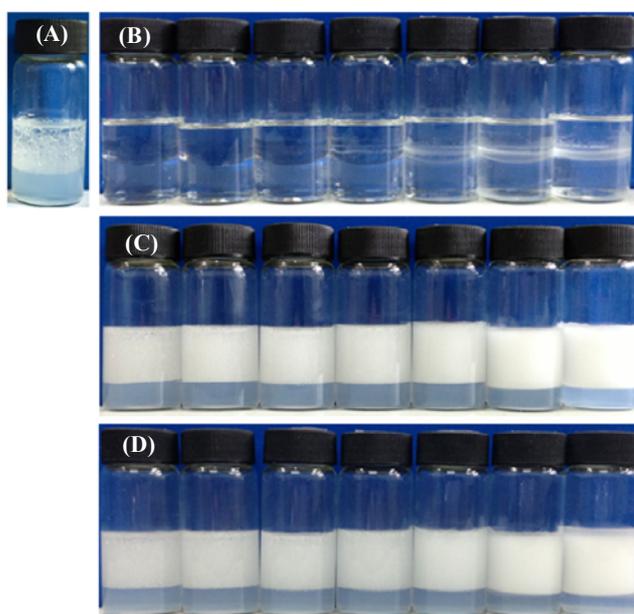


Figure 3. Optical micrographs of (A-E) toluene-in-water emulsion droplets stabilized by a mixture of 0.5 wt.% silica nanoparticles and different concentrations of $C_{12}E_5$ and (F) dodecane-in-water emulsion droplets stabilized by $C_{12}E_5$ alone taken 24 h after preparation. $[C_{12}E_5]/mM$ in water from A to F: 0.06, 0.1, 0.3, 0.6, 1 and 3. Temperature = 22 ± 2 °C.

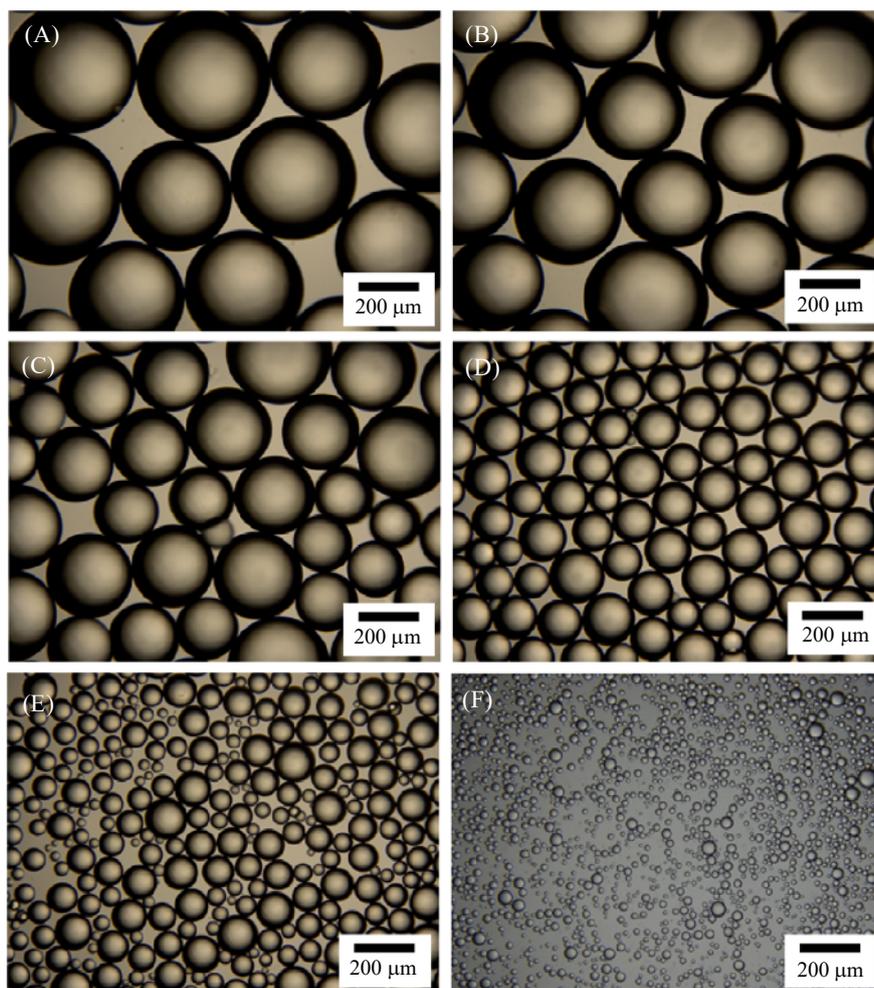


Figure 4. Time required for complete demulsification of a toluene-in-water emulsion stabilized by (a) mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₅ at different concentrations after warming to 45 °C with gentle stirring (100 rpm) and (b) 0.5 wt.% silica nanoparticles and 0.3 mM C₁₂E₅ after warming to different temperatures with gentle stirring (100 rpm).

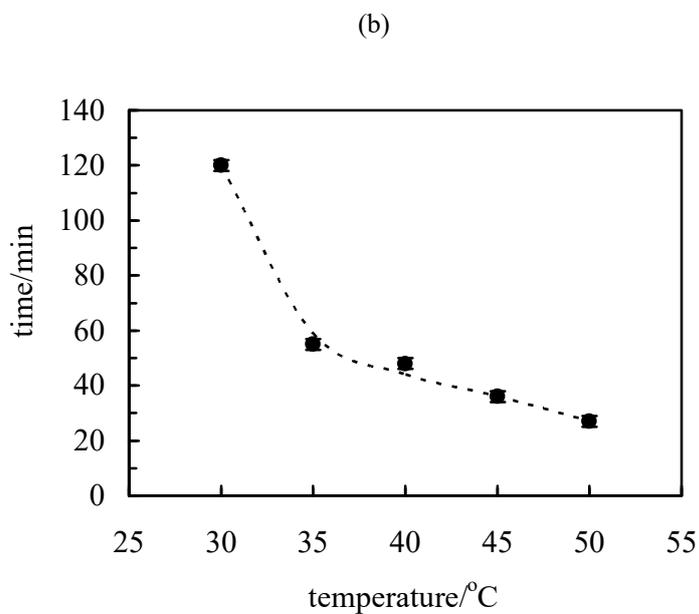
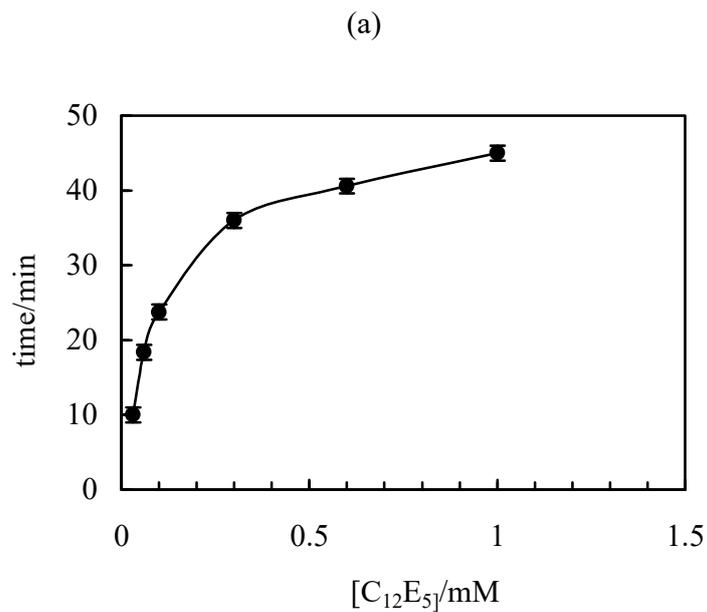


Figure 5. Photographs of (A) a toluene-in-water emulsion and (B) a dodecane-in-water emulsion stabilized by a mixture of 0.5 wt.% silica nanoparticles and 0.3 mM C₁₂E₅ following heating with stirring to 45 °C and cooling to 25 °C with re-homogenization for a number of cycles taken 24 h after preparation. (a) and (f) initial emulsion at 25 °C, (b) and (g) demulsified for the first time, (c) and (h) re-emulsified, (d) demulsified for the fifth time, (e) emulsified for the sixth time.

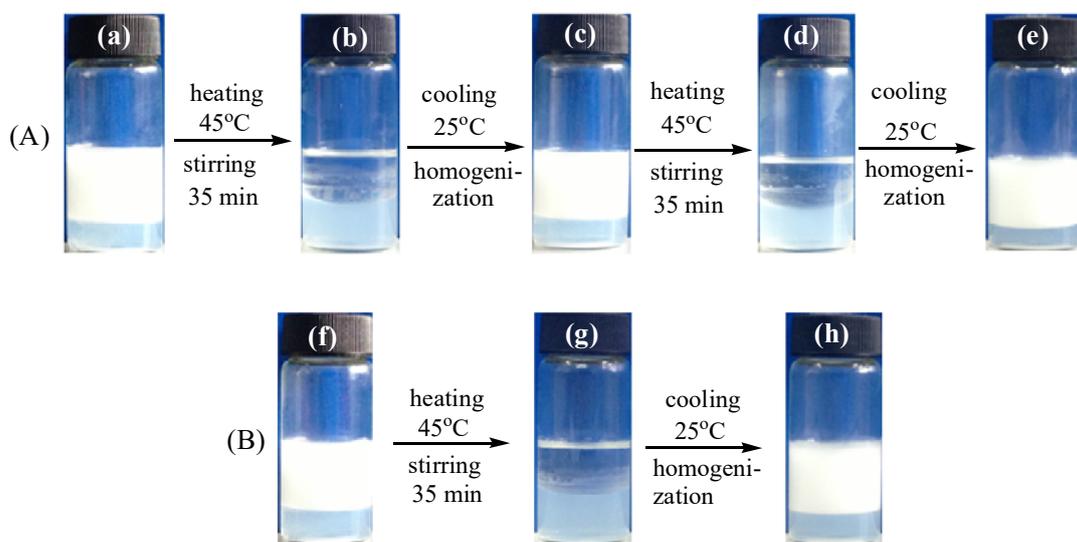


Figure 6. Optical micrographs of respective toluene-in-water emulsions shown in Figure 5 taken 24 h after preparation at room temperature (22 ± 2 °C). (a) Initial emulsion, (c) and (e) emulsion formed by homogenizing after demulsification once and six times, respectively.

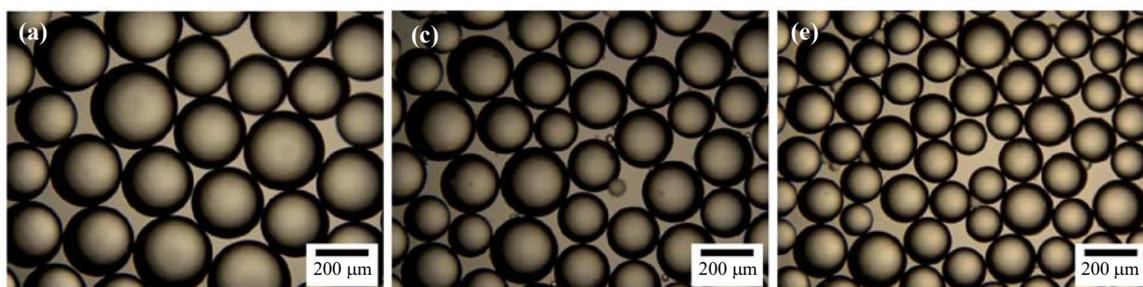


Figure 7. Photographs of toluene-in-water (7 mL/7 mL) emulsions stabilized by (A) C₁₂E₄ alone and (B) mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₄ at different concentrations taken 1 week after preparation at room temperature (22 ± 2 °C). [C₁₂E₄]/mM in oil from left to right: 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1, 3, 6 and 10. (C) Photographs of thermo-triggered demulsification/emulsification cycling of the emulsion stabilized by 0.5 wt.% silica and 6 mM C₁₂E₄ taken 24 h after operation; (left) initial emulsion at room temperature (22 °C), (middle) demulsified for the first time at 45 °C, (right) emulsified again at 25 °C.

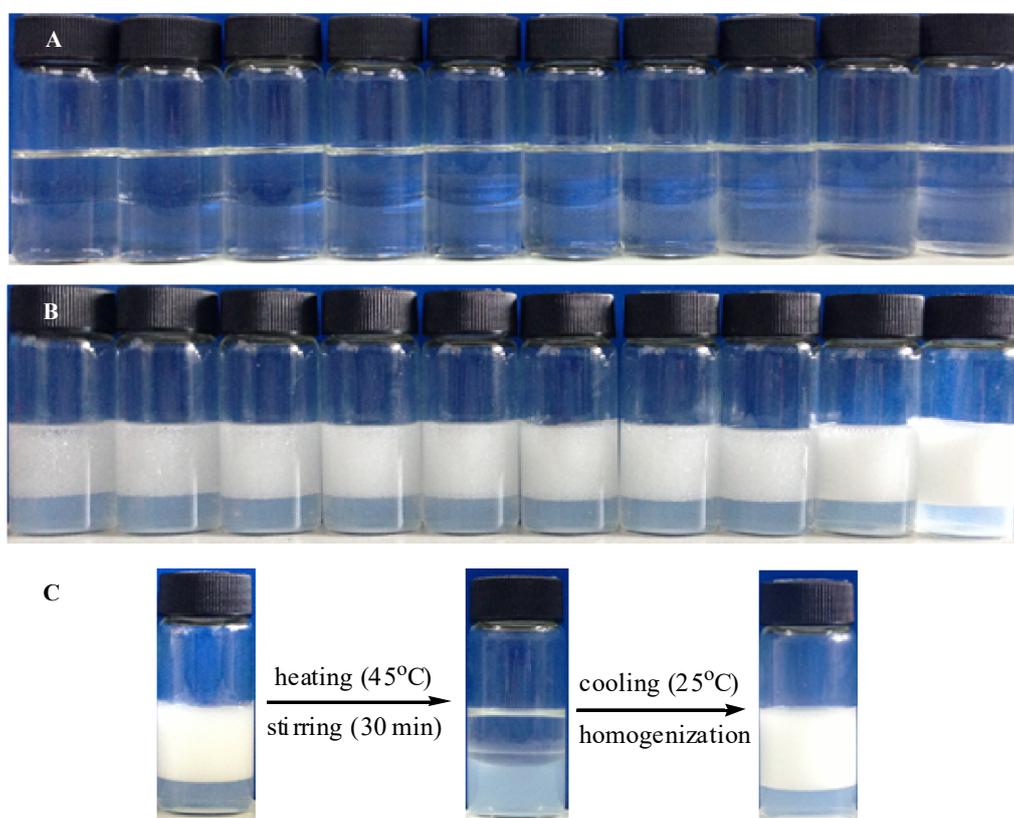


Figure 8. Photographs of toluene-in-water (7 mL/7 mL) emulsions stabilized by (A) C₁₂E₁₀ alone and (B) mixtures of 0.5 wt.% silica nanoparticles and C₁₂E₁₀ at different concentrations taken 1 week after preparation at room temperature (22 ± 2 °C). [C₁₂E₁₀]/mM in water from left to right: 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1 and 3. Micrographs of particle + surfactant emulsion (a-d) and emulsion of C₁₂E₁₀ alone (e) taken 24 h after preparation, as well as mixed emulsion (b') taken 4 h after being placed in a water bath at 45 °C with gentle stirring. [C₁₂E₁₀]/mM is (a) 0.06, (b), (b') 0.1, (c) (0.3), (d), (e) 1. (C) Photos of demulsification/emulsification cycling of an emulsion stabilized by 0.5 wt.% silica nanoparticles and 0.1 mM C₁₂E₁₀.

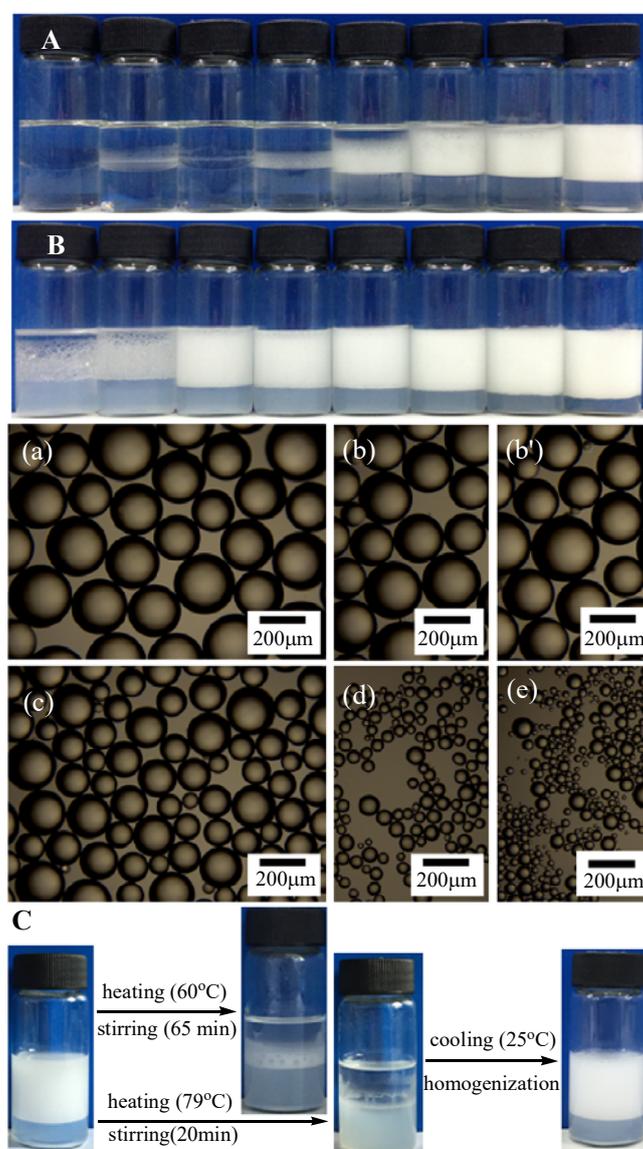


Figure 9. Micrographs of toluene-in-water Pickering emulsion droplets stabilized by 0.5 wt.% silica nanoparticles in combination with (a and b) 0.3 mM C₁₂E₅, (c) 0.6 mM C₁₂E₄ and (d) 0.3 mM C₁₂E₁₀ respectively, and toluene-in-water emulsion droplets stabilized by (e and f) 1 mM C₁₂E₁₀ alone at room temperature (22 ± 2 °C). (a) Partially dried Pickering oil droplet with wrinkled surface, (b-d) fully dried Pickering oil droplets displaying a surface shell with cracks and broken solid films, (e) fresh oil droplets with smooth surfaces and (f) oil droplets nearly fully dried exhibiting no surface shell.

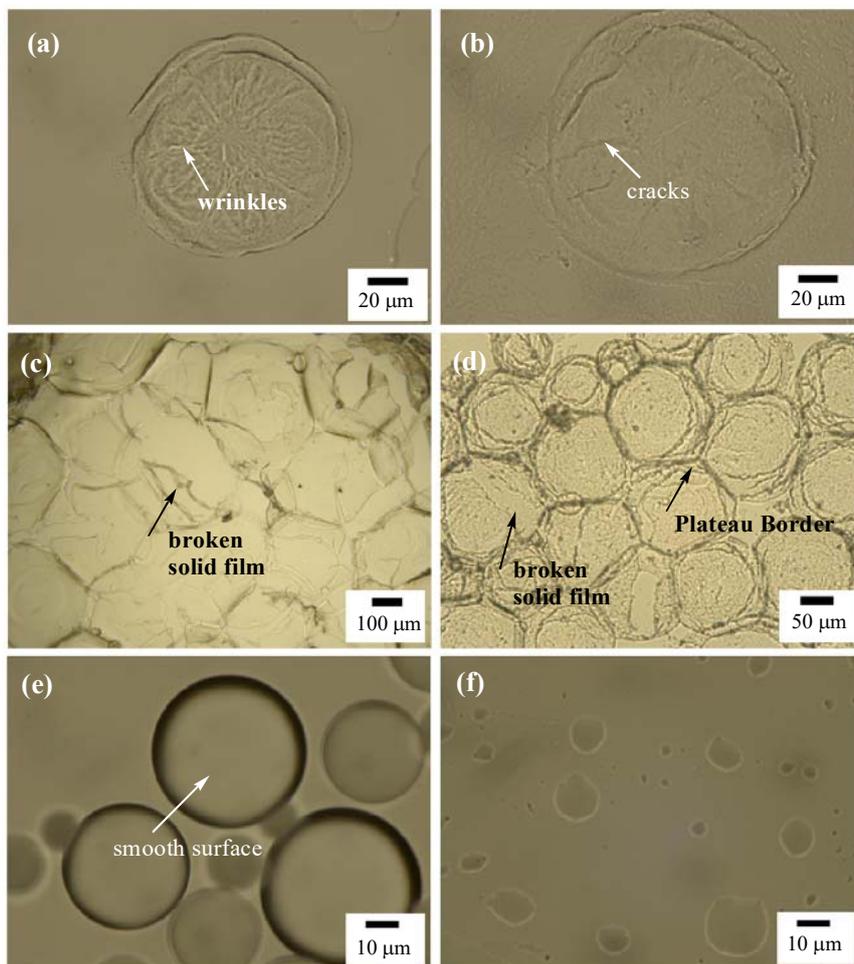
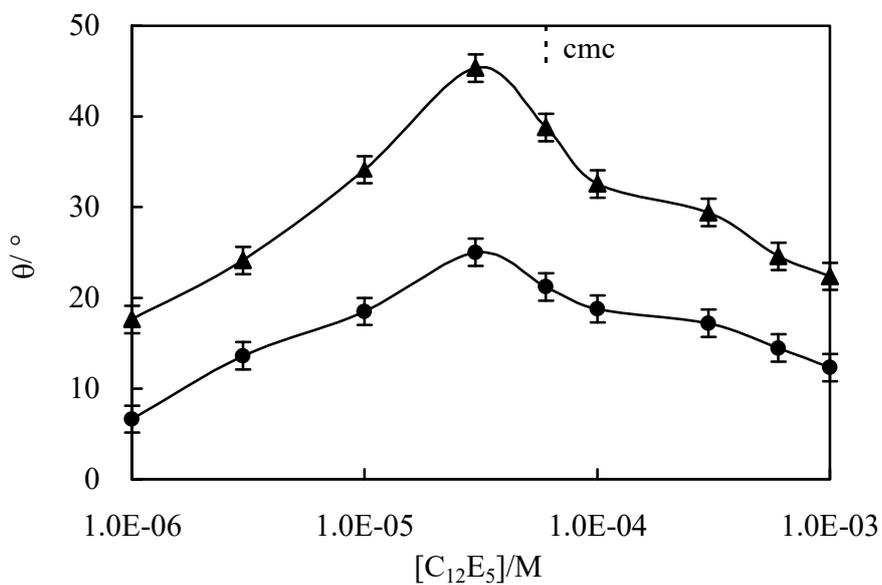


Figure 10. Contact angles of drops of aqueous $C_{12}E_5$ on a quartz slide in air (triangles) and contact angles through water of a toluene drop under an aqueous solution of $C_{12}E_5$ on a quartz slide (circles) as a function of the initial surfactant concentration in water at 25 °C. Toluene was pre-equilibrated with an equal volume of aqueous $C_{12}E_5$ solution for 24 h at 25 °C beforehand.



TOC graphic

