pH-responsive Pickering Emulsions Stabilized by Silica Nanoparticles in Combination with a Conventional Zwitterionic Surfactant

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Abstract

pH-responsive oil-in-water Pickering emulsions were prepared simply by using negatively charged silica nanoparticles in combination with a trace amount of a zwitterionic carboxyl betaine surfactant as stabilizer. Emulsions are stable to coalescence at pH ≤ 5 but phase separate completely at pH > 8.5. In acidic solution, the carboxyl betaine molecules become cationic allowing them to adsorb on silica nanoparticles *via* electrostatic interactions, thus hydrophobizing and flocculating them enhancing their surface activity. Upon increasing the pH, surfactant molecules are converted to zwitterionic form and significantly desorb from particles surfaces triggering de-hydrophobization and coalescence of oil droplets within the emulsion. The pH-responsive emulsion can be cycled between stable and unstable many times upon alternating the pH of the aqueous phase. The average droplet size in re-stabilized emulsions at low pH however increases gradually after four cycles due to the accumulation of NaCl. Experimental evidence including adsorption isotherms, zeta potentials, microscopy and three-phase contact angles is given to support the postulated mechanisms.

1. Introduction

The majority of Pickering emulsions stabilized by surface-active colloid particles are of superior stability to classical emulsions stabilized by surfactants or polymers [1-2]. However, when demulsification is needed, the ultra stability of Pickering emulsions can be challenging. Switchable or stimuli-responsive Pickering emulsions which can be transformed between stable and unstable by some simple triggers are therefore of interest, particularly for the cases where only temporarily stability is required such as in emulsion polymerization, fossil fuel production and oil transport. [3-4]

The preparation of switchable or stimuli-responsive emulsions relies on the development of corresponding switchable or stimuli-responsive stabilizers, which can be transformed between surface-active and surface-inactive *via* appropriate triggers. Currently several triggers have been developed, including pH, [5-20] temperature, [21-23] redox, [24] light irradiation, [25,26] CO_2/N_2, [27-35] magnetic field, [36,37] and dual triggers like pH-temperature, [38-41] light-temperature [42] and magnetic field intensity-temperature. [43,44]

Among these triggers, light irradiation and CO_2/N_2 triggers are environmentally benign. However, the efficiency of demulsification *via* light irradiation is normally low due to the turbidity or opacity of the emulsions, which blocks light transmission as a result of light scattering [3,4], and the CO_2/N_2 triggers involve not only complicated synthesis but also rigorous switching conditions like high or low temperatures [4]. The pH trigger, although relying on addition of acids and bases and suffering from accumulation of their neutralization products, is in general simple and easily realizable thanks to a breadth of chemicals and materials available [3] and is therefore still attractive.

Tang *et al.* [3] have recently reviewed the field of pH-responsive Pickering emulsions. The diverse pH-responsive Pickering emulsifiers are classified as unmodified organic [6,12] and inorganic [13,14] nanoparticles, covalent [15,16,] and non-covalent [17,18] surface functionalized nanoparticles, as well as self-assembled particles and micelles [11,19-20]. The wettability of these particulate emulsifiers is changed in response to protonation/deprotonation of the groups on the particle surface or the chemicals coated to the particle surface *via* various interactions. Since the accumulated products are neutral salts which in most cases are not hazardous to both the environment and the systems, the pH trigger is quite acceptable in cases where only one or limited cycles are expected. Nevertheless, the design and synthesis of the functional particles are in general complicated.

It has been reported that commercial inorganic nanoparticles which are originally surface-inactive can be made surface-active by *in situ* hydrophobization [45-47]. Here the particles are normally charged and highly water-wet in aqueous media, but once a trace amount of an oppositely charged amphiphile such as an ionic surfactant is present in water, the surfactant molecules adsorb at the particle-water interface with head-on configuration *via* electrostatic interaction. A hydrophobic monolayer is then formed at the solid-water interface which reduces the hydrophilicity of the particle surface enhancing the surface activity of the particles. If the *in situ* hydrophobization can be removed *via* some triggers, switchable or stimuli-responsive surface-active particles can be obtained. Based on this principle we have recently prepared switchable Pickering emulsions and foams with CO_2/N_2 trigger [4, 48] using silica nanoparticles in combination with a CO_2/N_2 switchable surfactant, and responsive Pickering emulsions and foams using silica nanoparticles in combination with a trace amount of conventional ionic surfactants triggered by ion-pair formation. [49, 50] The concentration of surfactant required is as low as 10% of the critical micelle concentration (cmc), which is economically beneficial for practical applications. In this paper we report on pH-responsive Pickering oil-in-water emulsions stabilized by silica nanoparticles in combination with a trace amount of a conventional alkyl carboxyl betaine surfactant. The latter is zwitterionic at neutral and alkaline pH range and does not induce significantly hydrophobization of the negatively charged silica nanoparticles, but hydrophobization is induced drastically at acidic pH where it is turned to cationic form and adsorbs significantly on particle surfaces. Both *n*-decane and toluene, representative of a non-polar and a polarisable hydrocarbon respectively, were used as the oil phase. The mixed Pickering emulsion is found to be stable at pH < 5 but unstable (demulsified) at pH > 8.5, and the involved mechanisms are discussed in detail.

2. Experimental

2.1 Materials

Silica nanoparticles (HL-200, 99.8%) with a primary particle diameter of 20 nm and a BET surface area of 200 ± 20 m^2/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. Silica microparticles of 99.9% purity with a primary diameter of 10 μm and a BET surface area of 0.81 m^2/g were purchased from Aladdin, China. Dodecyl dimethyl carboxyl betaine ($C_{12}H_{25}$-N^+-$(CH_3)_2$-CH_2-COO^-, $C_{12}B$) was synthesized in-house using dodecyl dimethyl amine from Solvay Specialty Chemicals Co. Ltd. *via* carboxylmethylation [51-52], and purified by re-crystallization from ethyl acetate followed by drying at vacuum below 60 °C. The purity of $C_{12}B$ was measured to be higher than 98% by two-phase titration using dimidium bromide-disulphine blue mixed indicators [53]. HPLC analysis and a mass spectrum of the product are shown in Figure S2. Sodium dodecyl sulfate (SDS) of 99% purity was purchased from Sigma. Hydrochloric acid (HCl, 36% in water) and sodium hydroxide (99%) were purchased from Sinopharm Chemical Reagent Co. *n*-Decane with a purity ≥ 98% and toluene of purity 99.5% were purchased from Aladdin and Sinopharm Chemical Reagent Co., respectively, and 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.

2.2 Preparation and characterization of emulsions

7 mL of aqueous phase with either surfactant or silica nanoparticles or both and 7 mL of oil phase (*n*-decane or toluene) were put in a 25 mL glass bottle (6.5 cm (h) by 2.5 cm (d)), followed by homogenization at 11,000 rpm for 2 min using an Ultra-Turrax homogenizer (IKA T18 basic, S18N-10G head). The concentration of particles and surfactant is expressed as weight percentage (wt.%) and moles per litre (mol/L) relative to the aqueous phase, respectively. The emulsion type was identified using the drop test, and photos of the emulsions at different time intervals and micrographs of fresh and dried emulsion droplets were recorded using a digital camera or a VHX-1000 microscope

system (Keyence Co.), respectively. The SEM image of dried emulsion droplets was obtained using a Hitachi S-4800 scanning electron microscope.

2.3 Switching on/off cycling of emulsions

Emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with a trace amount of $C_{12}B$ at $pH < 5$ (stable) were switched off (destabilized) by addition of 0.1 M aqueous NaOH solution raising the pH to > 8.5 followed by stirring with a glass rod or magnetic rotator. They were switched on (re-stabilized) by addition of 0.1 M aqueous HCl solution followed by homogenization at 11,000 rpm for 2 min. All experiments were carried out at room temperature (20-25 °C) unless specified otherwise.

2.4 Measurements

(a) pH of solutions, dispersions and emulsions

The pH of aqueous solutions, particle dispersions and emulsions was measured using a digital pH-meter (FE220, Mettler Toledo) at 25 ± 0.5 °C. The systems were allowed to settle for 24 h before measurement.

(b) Zeta potential of particles in water

0.01 ± 0.001 g of silica nanoparticles were weighed into a glass bottle (6.5 cm (h) × 2.5 cm (d), 25 cm^3), followed by adding 10 mL of either pure water or aqueous surfactant solution (particle concentration = 0.1 wt.%), adjusting the pH by adding aqueous HCl or NaOH (0.1M). 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. The dispersions were left for 24 h to reach adsorption equilibrium. The zeta potential of the silica nanoparticles was then measured at 25 °C using a ZetaPLAS instrument (Brookhaven), alongside the pH of the aqueous phase.

(c) Size of particles in water

Silica nanoparticles (0.1 wt.%) were dispersed in pure water or aqueous $C_{12}B$ solution of different concentration (neutral) using an ultrasound probe as described above, and the dispersions were left for 24 h to reach adsorption equilibrium at 25 °C. Then the diameter of the silica nanoparticles was measured at 25 °C using a ZetaPLAS instrument (Brookhaven). The dispersion was thoroughly shaken by hand before measurement.

(d) Surface tension

The air-water surface tensions of $C_{12}B$ solutions with and without silica nanoparticles were measured using the du Noüy ring method (home-built apparatus [46]) at 25 °C.

(e) Adsorption of surfactant at particle-water interface

The adsorption isotherms of $C_{12}B$ at the silica particle-water interface from aqueous dispersion were measured by depletion at 25 °C. 0.5 wt.% silica nanoparticles were dispersed in aqueous solutions of $C_{12}B$ of different concentration using an ultrasound probe (JYD-650, Shanghai) of tip diameter 0.6 cm operating at an output of 50 W for 1 min, and the dispersions were allowed to settle for 24 h at 25 °C. At equilibrium concentrations < cmc, the equilibrium concentration of $C_{12}B$ in the dispersion was obtained from the measured surface tension of the dispersion (measured without separating the particles) using the surface tension of the $C_{12}B$ solution without silica particles as calibration. At equilibrium concentrations > cmc, the equilibrium concentration was obtained by the two-phase mixed indicator titration, where silica nanoparticles were replaced by silica microparticles (diameter 10 μm) for separating particles from solution. 1.00 g of silica microparticles was dispersed in 10 mL of $C_{12}B$ solution and the dispersion was allowed to mix for 24 h using a rotating mixer followed by standing for 4 h at 25 °C. The supernatant separated was further centrifuged at 5,000 rpm for 20 min before being titrated.

(f) Contact angle at oil-water-glass interface

A quartz slide was cut into 1.5 cm wide strips, and the strips were soaked in a 30% aqueous NaOH solution for 24 h. They were then washed with pure water and dried in air. A clean strip was placed in a cubic cell (35mm (L) ×25mm (D) ×20mm (H)) with the two ends being supported by two standing legs. The cell was then filled with surfactant solution until the strip was immersed. After equilibrium (24 h), an *n*-decane drop was released from a U-shaped needle underneath the strip in solution, which was captured by the strip to form a reverse sessile drop. The contact angle of the oil drop through water was measured using a Dropmeter A-100 drop shape analyzer (Ningbo Haishu Maishi Scientific Test Co.). The temperature was kept at 25 ± 0.5 ºC using an air-therm heater (Air-Thermz-ATX, World Precision Instruments) during measurement.

3. Results and discussion

3.1 Pickering emulsions with neutral aqueous phase

Dodecyl dimethyl carboxyl betaine ($C_{12}B$) is a conventional zwitterionic surfactant, being cationic ($-N^+-CH_2-COOH$) at pH < pI (4.9-5.5) [54, 55] and zwitterionic at pH above this ($-N^+-CH_2-COO^-$), where pI is the isoelectric point [56]. The air-water surface tension curves of the surfactant at different pH are shown in Figure S2(c). The cmc is 1.4 mM [57] in pure water (pH = 6.1) and is little changed in acidic solution (pH = 4), although the surface tensions at concentrations < cmc are notably lower probably due to the synergism between the cationic and zwitterionic forms of the surfactant similar to in nonionic/ionic binary mixtures. For neutral pH of 6.1 where it is zwitterionic, at concentrations < cmc, $C_{12}B$ alone cannot stabilize *n*-decane-in-water emulsions as shown in Figure 1(A). Neither can the bare silica nanoparticles alone due to their extreme hydrophilicity, [4, 49] as seen in Figure 1(B, far left vessel). When silica nanoparticles (0.5 wt.%) coexist with $C_{12}B$ however, no stable emulsion was formed at $C_{12}B$ concentrations below 0.3 mM, but *n*-decane-in-water emulsions stable to coalescence were obtained at concentrations between 0.3 and 1 mM (< cmc), although creaming was not avoided as shown in Figure 1(B) and (C). For the stable emulsions, their appearance remained unchanged a week after preparation. Similar to the emulsions stabilized by silica nanoparticles hydrophobized *in situ* by other surfactants [4, 46, 49], the average droplet size was found to decrease with increasing $C_{12}B$ concentration (Figure 2(A-D)), and the droplets are much larger than those of emulsions stabilized by $C_{12}B$ alone at 3 mM (Figure 2(E)). In general, smaller droplet size endows better stability against creaming although the stability against coalescence is not significantly affected by droplet size. It is likely that the droplets are stabilised by surfactant-coated particles and particles being bigger than molecules results in larger drops in mixtures. Similar to other systems [4, 46, 49], the hydrophilic silica nanoparticles are hydrophobized *in situ* by $C_{12}B$ molecules *via* electrostatic interaction between its positive charge (N^+) and the negative charge on particle surfaces to endow surface activity, but the hydrophobization in neutral solution is weak as reflected by the high concentration of $C_{12}B$ required and the fact that no stable Pickering emulsion can be formed at low $C_{12}B$ concentration (< 0.3 mM).

3.2 Pickering emulsions with acidic aqueous phase

When the neutral aqueous phase was turned to acidic by adding aqueous HCl, no obvious influence of pH was observed with emulsions stabilized by 0.5 wt.% silica nanoparticles alone, or with those stabilized by $C_{12}B$ alone since the stabilization of $C_{12}B$ to the emulsions in either neutral or acidic aqueous medium is very similar, as shown in Figure 3(A) and (B). However, emulsions stabilized by silica nanoparticles together with $C_{12}B$ at concentrations below 0.3 mM were rendered stable. As an example, the appearance of batch emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM (<< cmc) $C_{12}B$ at different pH is shown in Figure 3(C) and (D). It can be seen that once the pH of the aqueous phase falls to ≤ 5.2, the emulsions become stable to coalescence and their average drop size decreases with decreasing pH (Figure 4). At pH = 3.6, the droplet sizes show no obvious change after 3 months, indicating ultra stability of the emulsion. It is thus without doubt that the hydrophobization of silica nanoparticles by $C_{12}B$ increases drastically upon lowering the pH.

Nevertheless the size of droplets (110-160 μm) shown in Figure 3(c) stabilized by

0.5 wt.% silica nanoparticles in combination with 0.06 mM $C_{12}B$ (0.043 cmc) is larger than that (40-70 μm) stabilized by 0.5 wt.% silica nanoparticles in combination with CTAB at similar relative concentration (0.03 mM, 0.033 cmc). [49] This is probably due to the longer alkyl chain in CTAB molecules than in $C_{12}B$ molecules, which increases the efficiency of the *in situ* hydrophobization by CTAB at similar adsorption levels. Besides, even in acidic pH, there is an equilibrium between the cationic and zwitterionic forms of $C_{12}B$ molecules and the zwitterionic form is less efficient than the cationic form in inducing hydrophobization.

3.3 Stabilization/destabilization cycling of Pickering emulsions responsive to pH

It is thus predicted that the Pickering emulsions stabilized by silica nanoparticles and a trace amount of $C_{12}B$ are pH-responsive, or can be cycled between stable and unstable by altering the pH. To prove this effect, an *n*-decane-water mixture stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM $C_{12}B$ was cycled by adding concentrated HCl (0.1 M) followed by homogenization and then adding concentrated NaOH (0.1 M) followed by agitation with a glass rod, as shown in Figure 5. In cycle 1, by adding HCl the pH of the aqueous phase was reduced to 4.39 and a stable oil-in-water emulsion was formed with drop diameters between 100 and 150 μm. Complete demulsification occurred within 20 min when the pH of the aqueous phase was increased to 8.84 by adding NaOH followed by agitation. This cycling can be repeated four times without any noticeable change in the average droplet size. In subsequent cycles however (5 to 7), demulsification was complete but the average droplet size gradually increased after homogenization at low pH. It may be that a build up of salt (NaCl) is responsible for this behavior (see later). For up to at least 7 cycles, the Pickering emulsion at pH = 4.4 was always ultra-stable, as reflected by a constant average droplet size over two months.

This pH-dependent behavior of the Pickering emulsions proved to be true also at a higher $C_{12}B$ concentration of 0.2 mM, as shown in Figure S3 where droplet sizes were found to be smaller. For example at pH = 3.6, the droplet sizes decrease to between 50 and 80 μm, approximately half that at 0.06 mM. Similarly, the emulsion can be cycled between stable and unstable (with complete demulsification) many times, with the droplet sizes showing an increase in the 4th cycle as shown in Figure S4.

3.4 pH-responsive Pickering emulsions for a different oil and surfactant

When *n*-decane was replaced by toluene, a polarisable aromatic hydrocarbon, similar pH-responsive Pickering emulsions were obtained stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM $C_{12}B$ as stabilizers, as shown in Figure 6(a). When the aqueous phase was neutral (pure water) no stable Pickering emulsion was formed. A stable emulsion formed by reducing the pH of the aqueous phase to 4.4 was then completely demulsified by increasing the pH subsequently to 9.4. It was re-stabilized upon lowering the pH to 4.4 with re-homogenization.

Similar pH-responsive behavior was also observed for *n*-decane-in-water Pickering emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM cetyl dimethyl carboxyl betaine ($C_{16}B$) which is more hydrophobic than $C_{12}B$, as shown in Figure 6(b). The emulsion was not stable in pure water, but a stable Pickering emulsion was formed when the pH was decreased to 4.2. This could then be demulsified by increasing the pH to 9.7 and re-stabilized by lowering the pH to 4.3. In this system, however, demulsification seems to be less complete as a thin layer of residual emulsion remains between the separated oil and aqueous phases.

3.5 Probing into the mechanism

As previously reported [4, 48-50] the silica nanoparticles are negatively charged at pH > 3 (Figure S5), and can then be hydrophobized *in situ* by adsorption of cationic surfactant *via* electrostatic interaction in water. The carboxyl betaine zwitterionic surfactants C_nB (n = 12-18) can adsorb at the silica nanoparticle-water interface [57] with head-on configuration (similar to cationic surfactants) at concentrations lower than the cmc even in neutral water (with pH > pI) so as to form a hydrophobic monolayer [58], since the positive and negative charges within the headgroup are separated and do not neutralize each other. Figure 7 shows the adsorption isotherms of $C_{12}B$ at the silica particle-water interface from aqueous media of different pH at 25 °C. Equilibrium concentrations lower than the cmc (1.4 mM in pure water) were measured by a surface tension method using silica nanoparticles [57] whilst those above the cmc were measured by two-phase titration using silica microparticles. It is observed that in pure water of pH = 6.1 the adsorbed amount of surfactant measured by the two different methods coincide well close to the cmc. The saturated value of 8.5×10^{-3} mmol/m^2 is comparable to that of 5.5×10^{-3} mmol/m^2 reported in the literature [59, 60] for a different silica sample. It corresponds to a cross-sectional area of 0.19 nm^2/molec. which is lower than that at the air-water interface at saturated monolayer adsorption (0.46 nm^2/molec.)[57], suggesting double layer or hemi-micelle formation. Figure 1 shows that in particle-surfactant mixtures, Pickering emulsions become stable to coalescence when the initial concentration of $C_{12}B$ is beyond 0.3 mM. The adsorbed amount on particle surfaces at this concentration (where equilibrium concentration = 0.26 mM) corresponds to an area per molecule of around 30 nm^2 which can be regarded as a critical value required for stabilization of the Pickering emulsion. Obviously in neutral media the adsorption of $C_{12}B$ at initial concentrations < 0.3 mM is too low to form a dense monolayer at particle surfaces and raise the particle hydrophobicity sufficiently.

By contrast, when the pH was reduced to 4, the adsorption isotherm moves upwards as seen in Figure 7. The critical adsorbed amount can now be achieved at an equilibrium concentration of 0.03 mM, approximately 1/10 of that at neutral pH. Therefore, as shown in Figure 3, emulsions stabilized with 0.5 wt.% silica nanoparticles and $C_{12}B$ at an initial concentration of 0.06 mM become stable at pH ≤ 5.2. At alkaline pH = 9, the adsorption isotherm is similar to that in pure water (Figure 7) and emulsions are similarly unstable. These results are in good agreement with reports in the literature that in neutral media the surfactant $C_{12}B$ adsorb at the silica-water interface with the quaternary nitrogen group N^+ close to the surface and the anionic COO^- group away from it, induced by a weak interaction between the hydrophilic group and the surface [59]. In acidic media, $C_{12}B$ molecules are mostly converted to the cationic form with much stronger electrostatic interaction with the surface [54].

Certain kinds of silica nanoparticles adsorb at the oil-water interfaces of emulsions as aggregates instead of primary particles [61]. This is the case here where, as shown in Figure S6, the average diameter of the silica nanoparticles dispersed in water of neutral pH before emulsification is around 230 nm *cf.* primary particle size of around 20 nm, and the aggregate size remains constant in solutions of $C_{12}B$ up to 1 mM. No flocculation of particles was observed as surfactant adsorption is too low at these concentrations (see later) in neutral media. But it is believed that the size of the aggregation is much larger in acidic media due to occurring of flocculation (Figure S7) (see later).

Particle adsorption to droplet interfaces is inferred from the loss of particles from water after emulsification, *i.e.* the aqueous phase becomes clear (see Figures 3, 5 and 6). The adsorption of the surfactant-coated particles at the oil-water interface is evidenced by the optical micrographs and SEM images of the emulsions stabilized by 0.5 wt.% silica in combination with 0.06 mM $C_{12}B$ at pH = 4, as shown in Figure 8. For a fresh toluene-in-water emulsion (A), droplets can be seen covered by wrinkled particle films which become solid films showing clear Plateau border and possessing cracks after evaporation of the solvents (B and C). Similarly a layer of broken solid film is clearly shown by the dried *n*-decane-in-water emulsion in (D).

The reduction of droplet size with increasing $C_{12}B$ concentration in both neutral and acidic media reflect an increase in the surface activity and adsorption at the oil-water interface of the silica nanoparticles. An increase in particle adsorption results in an increase of the total interface area and correspondingly a smaller droplet size [61]. It is likely that the particles or aggregates adsorbed at the oil-water interface are not “frozen” but rotate in the interface such that the sides facing oil have the opportunity to contact with H^+ and OH^- ions present in aqueous phase especially under stirring, so that they are responsive to the pH stimuli.

The *in situ* hydrophobization of the silica nanoparticles by $C_{12}B$, which is enhanced in acidic media and weakened in alkaline media, is also supported by the zeta potential measurements shown in Figure 9. The zeta potential of 0.1 wt.% silica nanoparticles dispersed in pure water (pH = 6.1) at 25 °C was -27.6 ± 0.3 mV (Figure S5). When dispersed in solutions of $C_{12}B$ in pure water, the zeta potential only increases slightly to -23.4 mV at 1.0 mM, in good agreement with the relatively low adsorbed amount and the zwitterionic character of the surfactant in neutral media. However, at low pH, surfactant molecules become cationic and neutralize the negative charges on particle surfaces by adsorption. The zeta potential thus increases significantly with $C_{12}B$ concentration, from -8.27 mV at 0.006 mM to +3.7 mV at 1.0 mM. In contrast, at high pH, the zeta potential which is more negative changes only slightly with $C_{12}B$ concentration. Photographs of the vessels containing silica nanoparticles dispersed in aqueous $C_{12}B$ solutions at low, neutral and high pH are given in Figure S7. Particles remain well dispersed at all surfactant concentrations in both neutral and alkaline media but flocculated [61] and sedimented in acidic media (floc diameter was several microns in 0.06 mM $C_{12}B$ at pH =4), in good agreement with the zeta potential findings. The positive zeta potentials of the particles at high $C_{12}B$ concentration at low pH suggests double or hemi-micelle adsorption of the $C_{12}B$ molecules, which may revert the wettability of particle surfaces to hydrophilic. The particles would thus tend to desorb from the oil-water interface resulting in demulsification of the Pickering emulsion. However, since the concentration of $C_{12}B$ is high enough to stabilize an emulsion alone, demulsification actually does not take place as shown in Figure 1 (B and C, vessels on far right) and Figure 2 (D). Instead, the Pickering emulsion is transformed to one stabilized by surfactant alone with particles collected in the aqueous films between drops or dispersed in the separated aqueous phase [45,46].

The effect of pH on the *in situ* hydrophobization of silica nanoparticles by $C_{12}B$ can also be probed by measurement of the oil-water-solid contact angle θ_{ow}, in which a quartz slide is used to mimic the silica particle surface. The slide is negatively charged and well wetted by pure water as reflected by a contact angle close to 0° (a spherical oil drop was obtained). The contact angles through water at two concentrations of $C_{12}B$ are shown in Figure 10 as a function of pH. θ_{ow} increases with a decrease in pH at both concentrations; *i.e.* surfaces become more hydrophobic in acidic media. This results in an increase in the surface activity of the coated silica nanoparticles compared with their behavior at neutral and alkaline pH. We also verified that at pH = 4, the contact angle passes through a maximum with respect to the concentration of $C_{12}B$, as it does for true cationic surfactants.

We noted earlier that the droplet size of the pH-responsive Pickering emulsions stabilized by silica nanoparticles and $C_{12}B$ surfactant gradually increases from cycle 5 (Figure 5). This effect can be explained as a result of the accumulation of NaCl following pH alternation by adding HCl and NaOH. Based on the amount of HCl and NaOH added, the concentration of NaCl produced increases by 1.6 mM for each cycle, so that by the 5th cycle the concentration reaches 6.4 mM. We carried out an experiment aimed to observe the effect of NaCl on the droplet size of the Pickering emulsion stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM $C_{12}B$ at pH = 4.4. The results, shown in Figure S8, show that the average droplet size does increase progressively upon increasing the salt concentration above 6.0 mM. It is also evident that more particles sediment in the aqueous phase with the build up of NaCl, reducing the amount adsorbing at droplet interfaces with a consequent increase in droplet size. This is caused by a decrease of the zeta potential of the particles in the presence of NaCl (but still negative), as shown in

Figure S9, which reduces the interaction between particles and $C_{12}B$ molecules in cationic form and thus the adsorption of the latter on the particles.

4. Conclusions

We have demonstrated that pH-responsive Pickering *n*-decane or toluene-in-water emulsions can be prepared by using negatively charged silica nanoparticles in combination with a trace amount of a conventional zwitterionic surfactant, dodecyltrimethyl carboxyl betaine. The emulsions are stable to coalescence at $pH \leq 5$ but can be demulsified completely at $pH > 8.5$. They can be cycled between stable and unstable by adding acid or base alternately. The adsorption of the cationic form of the surfactant at low pH on silica particle surfaces induces sufficient hydrophobization *in situ* and flocculation of particles endowing surface activity to the particles. However, the droplet size increases gradually after several cycles due to the accumulation of salt in the system, which partially screens the electrostatic interaction between the positively charged carboxyl betaine molecules and the negatively charged particle surfaces.

Keywords: pH-responsive, Pickering emulsions, silica nanoparticles, carboxyl betaine, hydrophobization, adsorption, zeta potential.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

SEM and TEM images of powdered silica nanoparticles of HL-200, HPLC analysis, mass spectrum, as well as surface tension curves at different pH of $C_{12}B$, photographs and micrographs of *n*-decane-in-water batch emulsions stabilized by a mixture of 0.5 wt.% silica nanoparticles and 0.2 mM $C_{12}B$ at different pH, photographs and micrographs of *n*-decane-in-water emulsions stabilized by 0.5 wt.% silica nanoparticles and 0.2 mM $C_{12}B$ following pH alternation, zeta potentials of silica nanoparticles dispersed in water of different pH, average diameter of silica nanoparticles (0.1 wt.%) dispersed in aqueous solutions of $C_{12}B$ at different concentrations (neutral pH), photographs of vessels containing 0.1 wt.% silica nanoparticles dispersed in aqueous solutions of $C_{12}B$ at different pH as a function of $C_{12}B$ concentration, photographs and micrographs of *n*-decane-in-water emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM $C_{12}B$ at pH = 4.4 in the presence of NaCl of different concentration, and effect of NaCl concentration on the zeta potential of 0.1 wt.% silica nanoparticles dispersed in water of pH = 4.4 at 25 °C (PDF).

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Captions

Figure 1. Photographs of *n*-decane-in-water of pH = 6.1 (7 mL/7 mL) emulsions stabilized by $C_{12}B$ alone at different concentrations (A) and by mixtures of 0.5 wt.% silica nanoparticles and $C_{12}B$ at different concentrations (B, C) taken 24 h (A, B) and 1 week (C) after preparation. [$C_{12}B$]/mM in water from left to right: (A) 0.006, 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1, 3 and 6; (B, C) 0, 0.006, 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1 and 3.

Figure 2. Optical micrographs of *n*-decane-in-water (pH = 6.1) emulsions stabilized by a mixture of 0.5 wt.% silica nanoparticles and $C_{12}B$ at different concentrations (A−D) and by $C_{12}B$ alone (E) taken 24 h after preparation. [$C_{12}B$]/mM from A to E: 0.3, 0.6, 1, 3 and 3.

Figure 3. Photographs of *n*-decane-in-water (7 mL/7 mL) batch emulsions stabilized by 0.5 wt.% silica nanoparticles alone (A), 0.06 mM $C_{12}B$ alone (B) and a mixture of 0.5 wt.% silica nanoparticles and 0.06 mM $C_{12}B$ (C-D) at different pH as shown above the vessels (vessel 1 in (C-D) is pure water), respectively, taken 24 h (A-C) and 3 months (D) after preparation.

Figure 4. Optical micrographs of decane-in-water emulsions containing 0.5 wt.% silica nanoparticles and 0.06 mM $C_{12}B$ at pH stated 24 h (A-C) and 3 months (D) after preparation.

Figure 5. Photographs and optical micrographs (low pH only) of *n*-decane-in-water emulsions stabilized by a mixture of 0.5 wt.% silica nanoparticles and 0.06 mM $C_{12}B$ following pH alternation by adding 0.1 M HCl and 0.1 M NaOH, taken 24 h and 2 months (cycle 7 only) after preparation.

Figure 6. Appearance of (a) toluene-in-water and (b) *n*-decane-in-water (7 mL/7 mL) emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with (a)

0.06 mM $C_{12}B$ and (b) 0.06 mM $C_{16}B$ following switching between stable at low pH and unstable at high pH, taken 24 h (stable) and 30 min (unstable) after addition of HCl/NaOH.

Figure 7. Adsorption isotherms of $C_{12}B$ at negatively charged silica particle-water interfaces from water of different pH at 25 °C.

Figure 8. Optical micrograph (A, fresh) and SEM images (B, C, dried) of toluene-in-water emulsion and optical micrograph (D, dried) of *n*-decane-in-water emulsion stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM $C_{12}B$ at pH = 4.

Figure 9. Zeta potential of 0.1 wt.% silica nanoparticles dispersed in aqueous solutions of $C_{12}B$ at different pH as a function of initial $C_{12}B$ concentration at 25 °C.

Figure 10. Contact angle through water of drops of *n*-decane in aqueous $C_{12}B$ at two concentrations on a negatively charged quartz slide as a function of pH at 25 °C. Error bar is ± 3°.

Figures

Figure 1. Photographs of *n*-decane-in-water of pH = 6.1 (7 mL/7 mL) emulsions stabilized by $C_{12}B$ alone at different concentrations (A) and by mixtures of 0.5 wt.% silica nanoparticles and $C_{12}B$ at different concentrations (B, C) taken 24 h (A, B) and 1 week (C) after preparation. [$C_{12}B$]/mM in water from left to right: (A) 0.006, 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1, 3 and 6; (B, C) 0, 0.006, 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1 and 3.

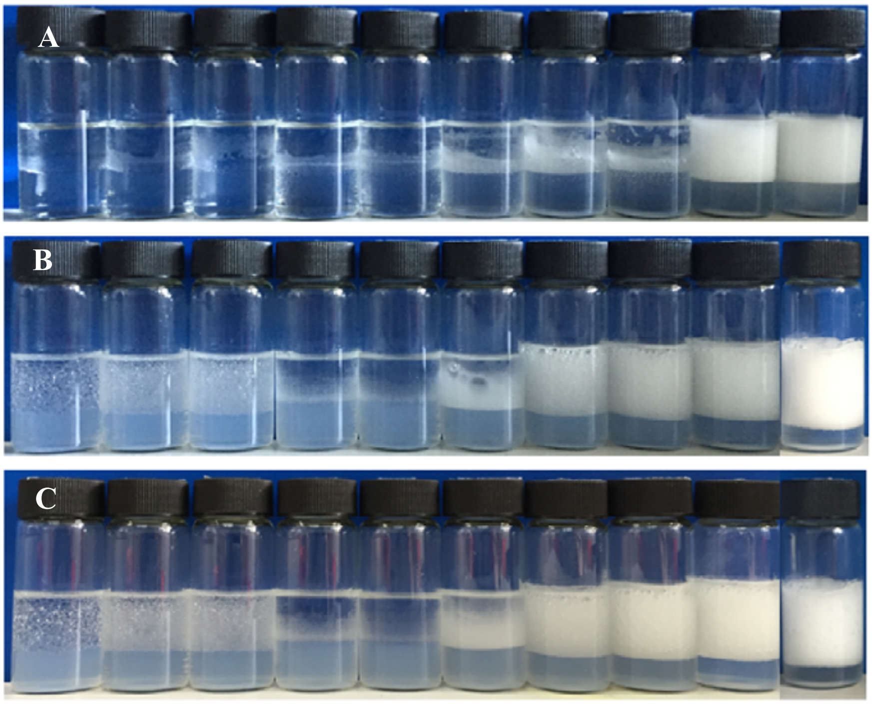
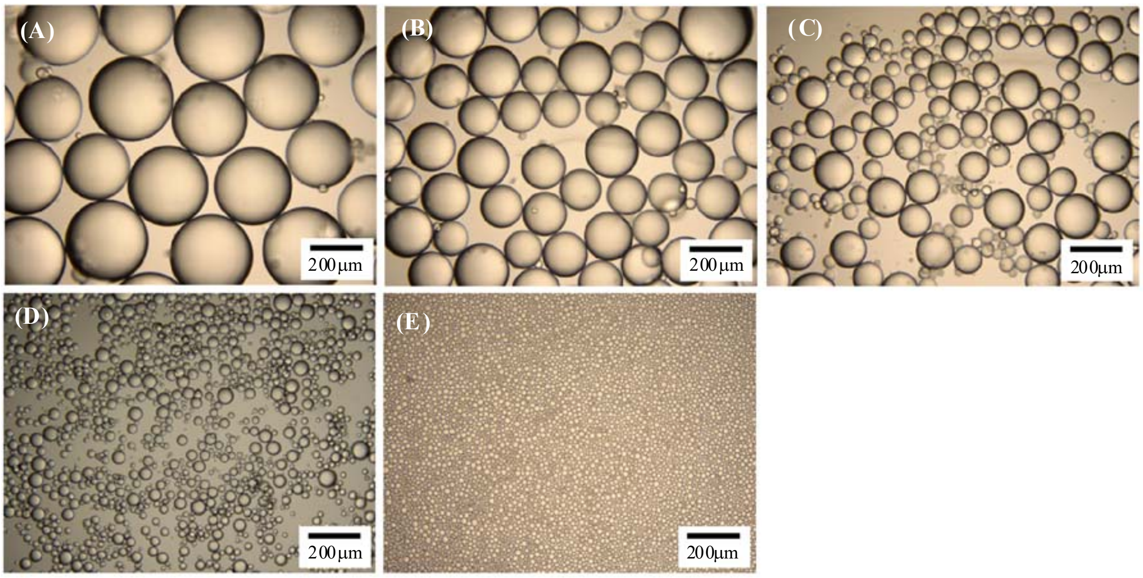


Figure 2. Optical micrographs of *n*-decane-in-water (pH = 6.1) emulsions stabilized by a mixture of 0.5 wt.% silica nanoparticles and $C_{12}B$ at different concentrations (A−D) and by $C_{12}B$ alone (E) taken 24 h after preparation. [$C_{12}B$]/mM from A to E: 0.3, 0.6, 1, 3 and 3.



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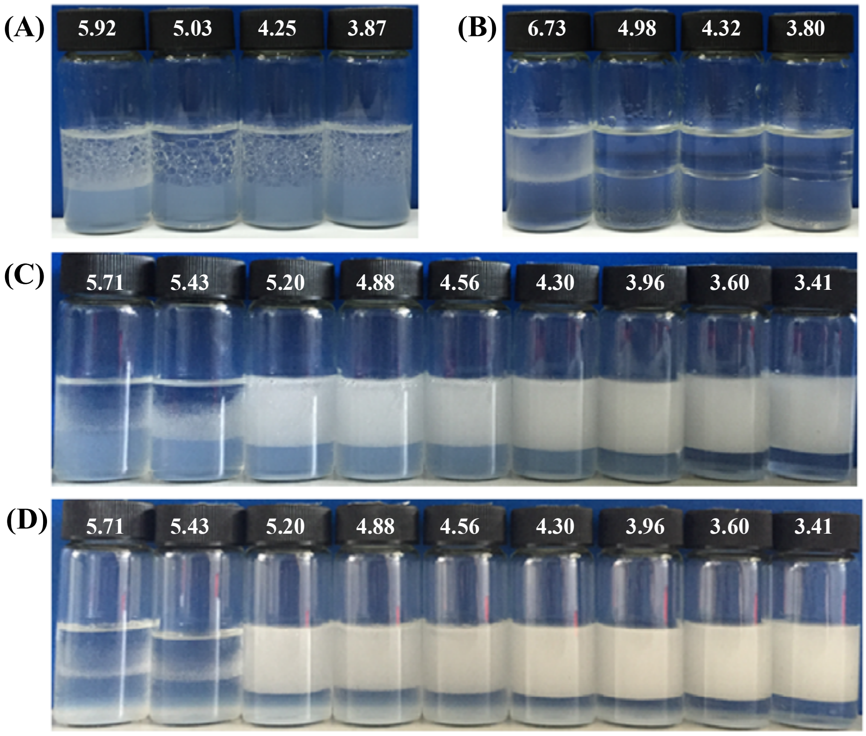

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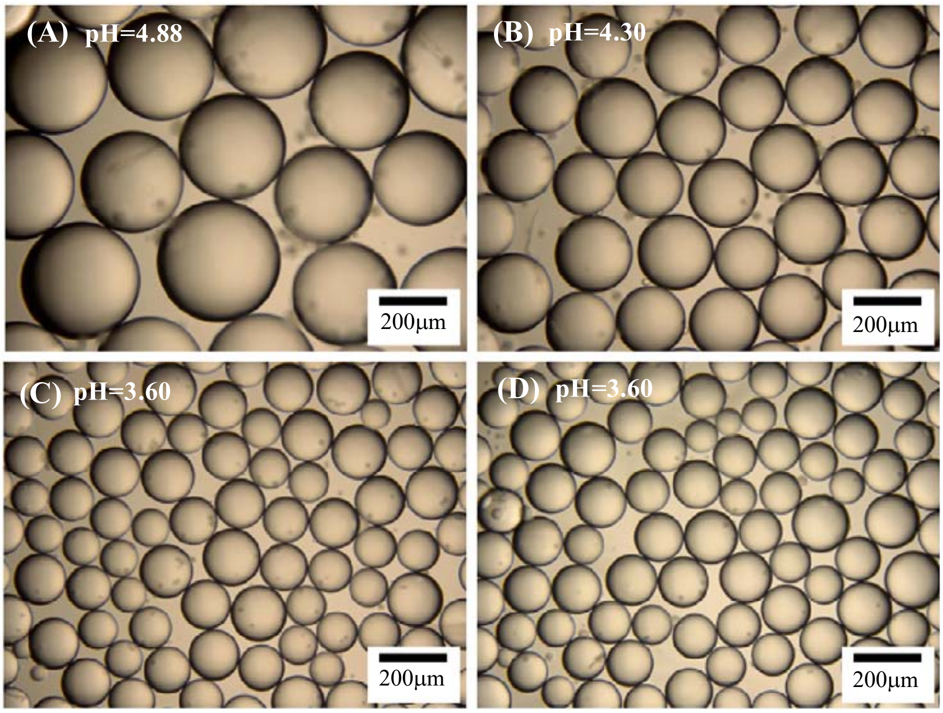
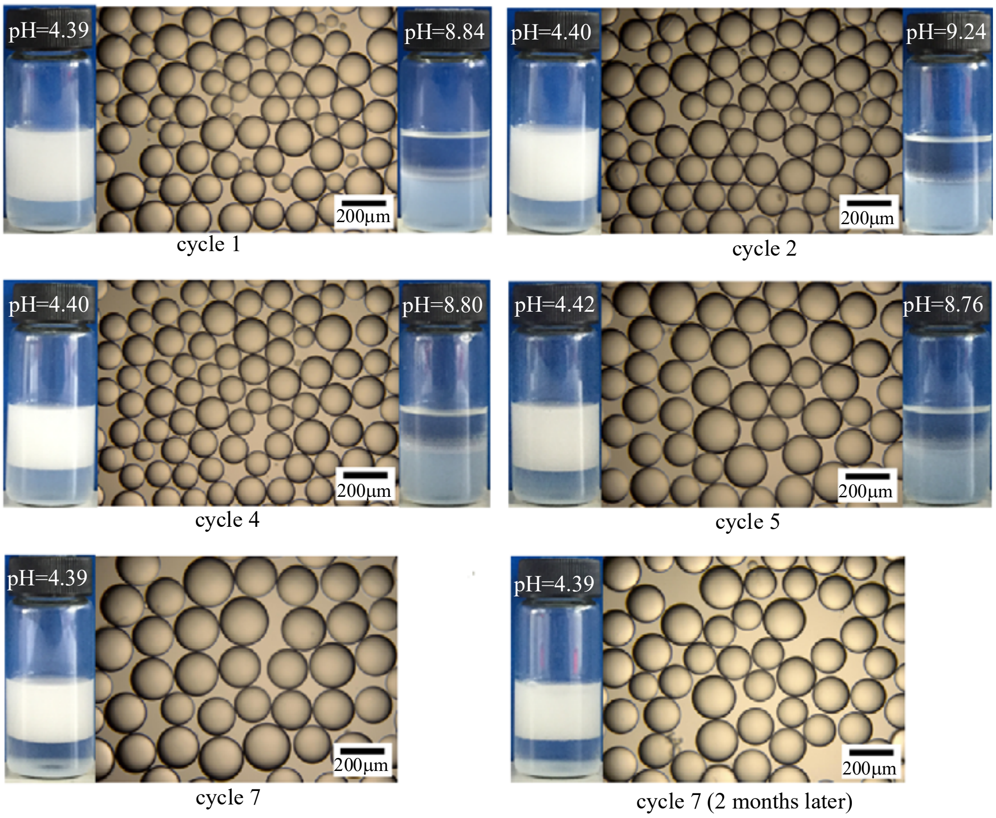


Figure 5. Photographs and optical micrographs (low pH only) of *n*-decane-in-water emulsions stabilized by a mixture of 0.5 wt.% silica nanoparticles and 0.06 mM $C_{12}B$ following pH alternation by adding 0.1 M HCl and 0.1 M NaOH, taken 24 h and 2 months (cycle 7 only) after preparation.



cycle 1

cycle 2

cycle 4

cycle 5

cycle 7

cycle 7 (2 months later)

Figure 6. Appearance of (a) toluene-in-water and (b) *n*-decane-in-water (7 mL/7 mL) emulsions stabilized by 0.5 wt.% silica nanoparticles in combination with (a) 0.06 mM $C_{12}B$ and (b) 0.06 mM $C_{16}B$ following switching between stable at low pH and unstable at high pH, taken 24 h (stable) and 30 min (unstable) after addition of HCl/NaOH.

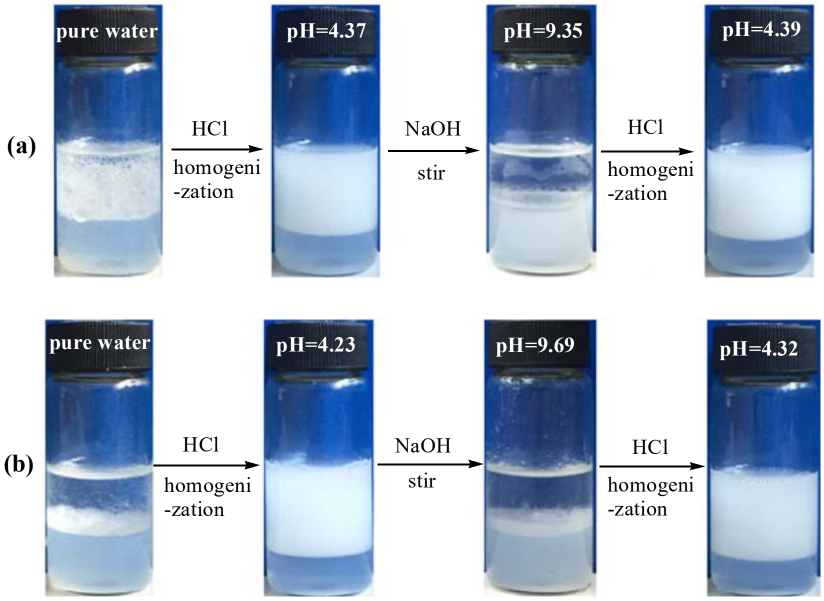
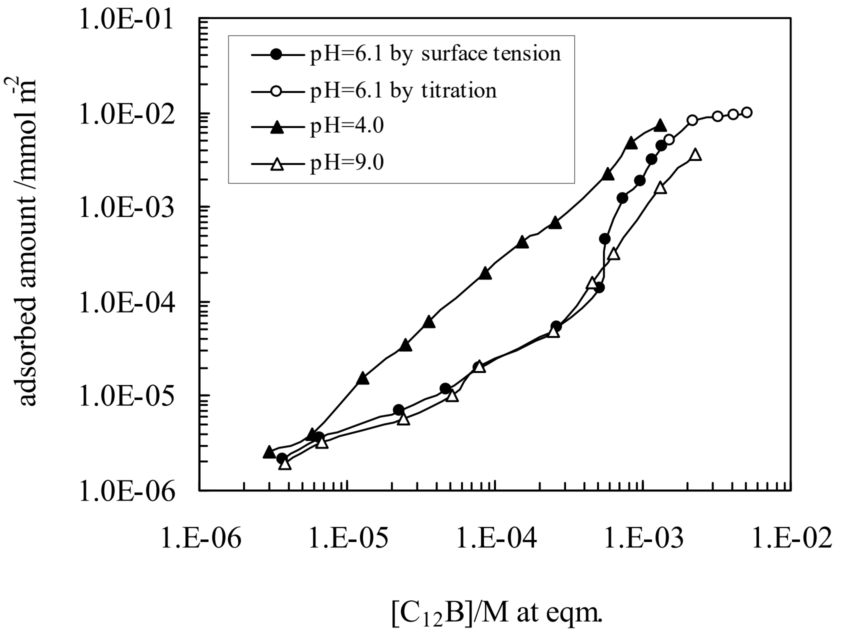


Figure 7. Adsorption isotherms of $C_{12}B$ at negatively charged silica particle-water interfaces from water of different pH at 25 °C.



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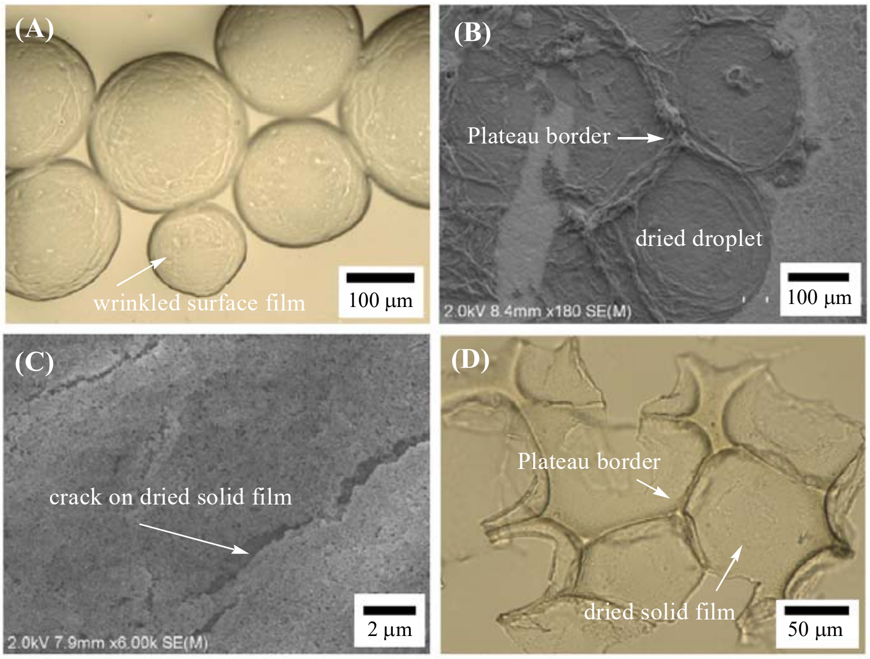
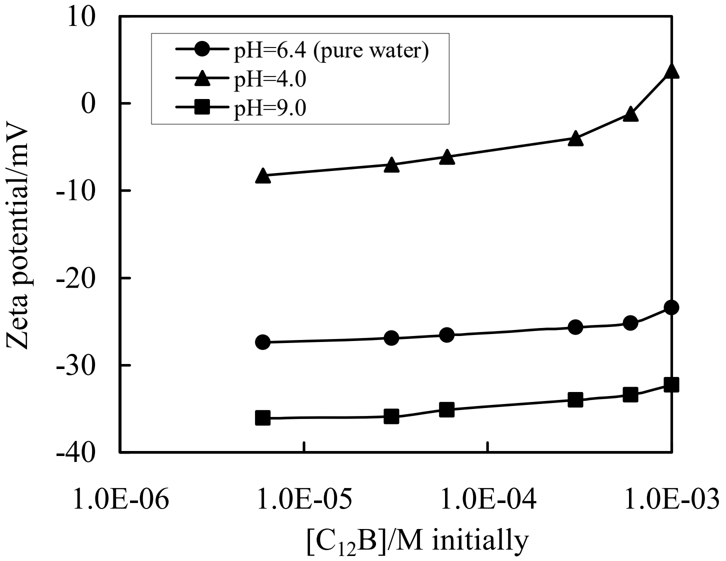


Figure 9. Zeta potential of 0.1 wt.% silica nanoparticles dispersed in aqueous solutions of $C_{12}B$ at different pH as a function of initial $C_{12}B$ concentration at 25 °C.



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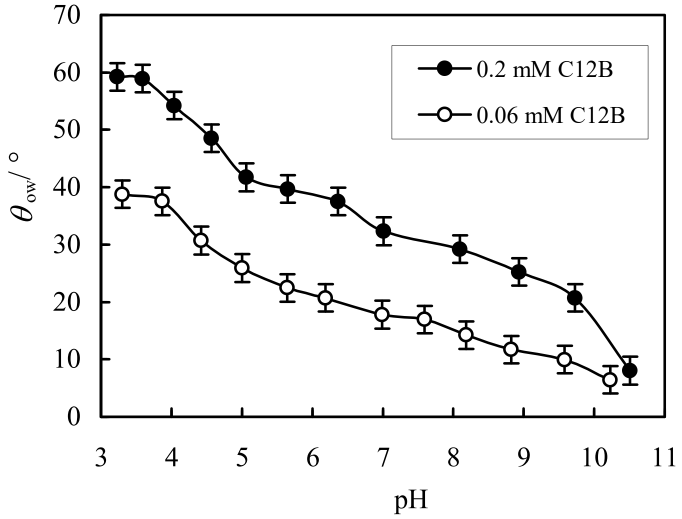
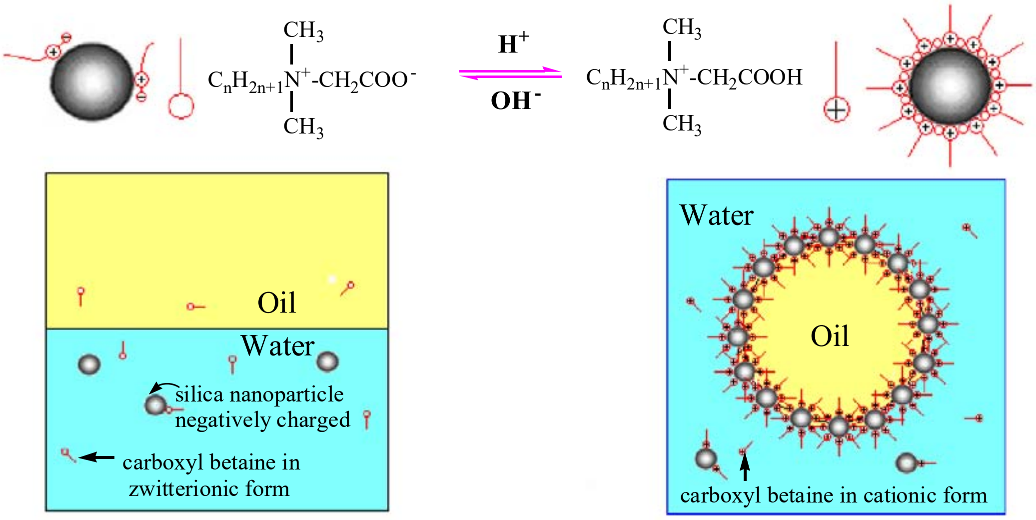


TOC Graphic


CH3
CnH2n+1N+-CH2COO-
CH3
H+
OH-
CH3
CnH2n+1N+-CH2COOH
CH3
Oil
Water
silica nanoparticle negatively charged
carboxyl betaine in zwitterionic form
Water
Oil
carboxyl betaine in cationic form