CO₂/N₂ triggered switchable Pickering emulsions stabilized by alumina nanoparticles in combination with a conventional anionic surfactant

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Stable n-decane-in-water Pickering emulsions were prepared using positively charged alumina nanoparticles in combination with a trace amount of the anionic surfactant sodium dodecyl sulfate (SDS) as a stabilizer. Particles were hydrophobized in situ by adsorption of surfactant enhancing their surface activity. Emulsions can be readily demulsified by addition of an equal amount of a switchable surfactant, N'-dodecyl-N,N-dimethylacetamidine (DDAA), which can be transformed between a surface-active amidinium/cationic form and a surface-inactive amidine/neutral form by bubbling CO₂ or N₂, respectively. Following addition of cationic DDAA which prefers to form ion pairs with SDS, desorption of SDS from particle surfaces occurs and alumina particles are rendered hydrophilic resulting in demulsification of the emulsion. However, by bubbling N₂ into the demulsified mixture, DDAA molecules are converted to the amidine/neutral form leading to collapse of the ion pairs and re-establishment of the in situ hydrophobization of particles. Stable Pickering emulsions can be prepared again following homogenization. This simple demulsification/re-stabilization cycle can be repeated several times. Experimental evidence including measurement of the adsorption isotherm, zeta potentials, extent of particle adsorption at droplet interfaces in emulsions and microscopy is given to support the postulated mechanisms.

1. Introduction

It is well known that Pickering emulsions stabilized by surface-active colloid particles have usually very good long term stability,2–13 in contrast to conventional emulsions stabilized by surfactants or polymers which are kinetically stable.4 On the other hand, however, demulsification of Pickering emulsions is relatively difficult due to the high desorption energy of particles from the oil–water interface,4,12 which is a challenge in cases where only temporary stability is required such as in emulsion polymerization, oil transport and fossil fuel production.5–6 Switchable or stimuli-responsive Pickering emulsions which can be transformed between stable and unstable by some simple triggers are therefore of interest and have received recent attention.5

It is obvious that the formation of switchable or stimuli-responsive emulsions relies on developments in the corresponding particulate stabilizers, which can be transformed between surface-active and surface-inactive via appropriate triggers.4,14 For this purpose particles have to be coated or grafted with functional groups which can be transformed between hydrophilic and lipophilic in response to appropriate triggers.5 Currently several triggers have been developed, including light irradiation,7–10 CO₂/N₂,11–14 temperature,15–17 pH,18–24 redox,25,26 magnetic field,27,28 and dual triggers like pH–temperature,29,30 light–temperature31 and magnetic field intensity–temperature.32 Among these triggers, the pH and redox triggers require addition of chemicals which accumulate in the system and may produce unexpected effects on products especially in systems undergoing multiple cycles.5 These triggers however are convenient to achieve with a variety of suitable chemicals. Light irradiation is environmentally benign, but the efficiency of demulsification may be significantly inhibited by the turbidity or opacity of the emulsions.6 The temperature trigger which avoids addition of chemicals is a good choice in cases where the products are thermo-resistant and the energy consumption is not a problem. The CO₂/N₂ trigger originally developed for surfactants33–35 is more attractive and has been extended to colloidal particles4,11–14 since both CO₂ and N₂ are environmentally benign and there is no accumulation in systems after
use. Rigorous switching conditions however are sometimes required such as very low or high temperature. Tang et al. have recently reviewed the different triggers applicable to Pickering emulsions including their advantages and disadvantages. Nevertheless the design and synthesis of these 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. A typical example is silica nanoparticles which are negatively charged in neutral water and can be hydrophobized in situ by a trace amount of cationic surfactant. The positively charged surfactant ions adsorb at the particle–water interface via electrostatic interaction with head-on configuration, forming a hydrophobic monolayer on particle surfaces increasing the particle hydrophobicity and thereby endowing particles with surface activity. The coated particles can then assemble at either oil–water or air–water interfaces to stabilize Pickering emulsions and foams respectively. Moreover the wettability or surface activity of the particles can be controlled by adjusting the length and/or the number of the surfactant alkyl chain(s) as well as the concentration of surfactant enabling stabilization of either oil-in-water (o/w) or water-in-oil Pickering emulsions along with emulsion phase inversion. In systems where the in situ hydrophobization can be removed via some triggers, switchable or stimuli-responsive surface-active particles can be obtained. Using this protocol we have recently prepared switchable Pickering emulsions and foams with the CO2/N2 trigger using silica nanoparticles in combination with a CO2/N2 switchable surfactant. In addition, stimuli-responsive Pickering emulsions and foams were demonstrated triggered by ion pair formation and pH using silica nanoparticles in combination with conventional cationic/anionic and zwitterionic surfactants. In all cases the concentration of surfactant required is as low as 10% of the critical micelle concentration (cmc), which is economically beneficial for practical applications.

In contrast to silica nanoparticles, alumina nanoparticles are positively charged in neutral water and there is no direct interaction between them and the CO2/N2 switchable surfactants. On the other hand it is possible to hydrophobize in situ these nanoparticles using anionic amphiphiles such as anionic surfactant, short chain fatty acids and functional polymers to endow them with surface activity. In this paper we report on CO2/N2 triggered switchable Pickering emulsions prepared by using positively charged nanoparticles in combination with the anionic surfactant sodium dodecyl sulfate (SDS) and equal moles of the switchable surfactant N-dodecyl-N,N-dimethylacetamidine (DDAA). In neutral water, alumina nanoparticles are hydrophobized in situ by adsorption of SDS enabling them to adsorb at the oil–water interface and stabilize an o/w emulsion. Once DDAA in amidinium/cationic form is added into the emulsion, it prefers to form ion pairs with SDS via electrostatic attraction. SDS ions desorb from particle surfaces reversing their hydrophobization resulting in demulsification of the emulsion. However, upon bubbling N2 into the demulsified system, DDAA molecules are converted to the amine/neutral form. The ion pairs disassemble and the in situ hydrophobization of particles is re-established such that a stable Pickering emulsion is reformed following re-homogenization. Demulsification can be achieved again by bubbling CO2 into the system. This demulsification/re-stabilization cycle can be realized several times without any detrimental effects on the emulsion.

2. Experimental

2.1 Materials

Hydrophilic alumina (Al2O3) nanoparticles with a purity of >99.8 wt% were purchased from Sigma. Their primary particle diameter is 13 nm with a surface area of 85–115 m2 g⁻¹ according to the supplier. Electron microscopy images of the particles are shown in Fig. S1. Sodium dodecyl sulfate (SDS) with a purity >99% was purchased from Sigma. N'-Dodecyl-N,N-dimethylacetamidine (DDAA) was synthesized in-house and was purified by passing through a column filled with silica resulting in a purity >98%. It can be converted to N'-dodecyl-N,N-dimethylacetamidinium bicarbonate by bubbling CO2 in pure water at low temperature 0–5 °C. n-Decane and n-hexane with a purity of >98% were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd., China. Ultrapure water with a resistance of 18.2 MΩ cm and a pH of 6.1 was produced from a Simplicity Pure Water System (Merck Millipore, Shanghai). All other chemicals used were analytically pure and were purchased from Sinopharm Chemical Reagent Co. They were used as received unless specified.

2.2 Preparation and characterization of emulsions

A known mass of alumina nanoparticles was weighed into a glass bottle of 25 mm (d) × 65 mm (h) of volume 25 mL. 7 mL of either pure water or aqueous SDS solution was added, followed by ultrasonic dispersing at an output of 50 W for 1 min using an ultrasound probe (JYD-650, Shanghai) of tip diameter 0.6 cm. Then 7 mL of oil (n-decane) was added and the mixture was homogenized using an ultraturrax homogenizer (IKA T18 basic, S18N-10G head) at 11 000 rpm for 2 min, with the emulsion type being identified by the drop test. The concentration of alumina and surfactant is expressed as weight percentage (wt%) and moles per liter (mol L⁻¹) in the aqueous phase respectively. Emulsions were allowed to stand at room temperature to observe their stability by taking photographs of the vessels and micrographs of the droplets using a VHX-1000 microscope system (Keyence Co.). In systems without particles, oil was directly emulsified with surfactant solution as described above.

2.3 Demulsification/re-stabilization cycle of the Pickering emulsions

A stable n-decane-in-water (7 mL/7 mL) Pickering emulsion stabilized by 0.5 wt% alumina nanoparticles in combination with 0.3 mM SDS was prepared in the container of a glass bubbling device shown in Fig. S2 as described above. Then DDAA in amidinium/cationic form of equal moles to SDS in the emulsion was added as a concentrated aqueous solution (30
25 mM to induce demulsification. The phase separated demulsified system was then bubbled with N₂ at 65 °C for 80 min at a flow rate of 160 mL min⁻¹ followed by homogenization to form a stable Pickering emulsion. This latter emulsion was subsequently bubbled with CO₂ at 0–5 °C for 80 min at a flow rate of 160 mL min⁻¹ to induce demulsification. In this way, the demulsification/re-stabilization cycle of the Pickering emulsion was effected by alternately bubbling with CO₂ and N₂ followed by homogenization.

2.4 Measurements

(a) pH, zeta potential and particle size. 0.1 wt% alumina nanoparticles were dispersed ultrasonically in pure water of different pH (adjusted with HCl or NaOH) or in aqueous solution of surfactant. The dispersions were allowed to stand for 24 h to reach equilibrium. The pH of the dispersions was measured using a digital pH-meter (FE220, Mettler Toledo) at 25 °C, and the zeta potentials as well as the size of the particles were measured using a ZetaPLAS instrument (Brookhaven) also at 25 °C.

(b) Surface tension of solution or dispersion. The surface tension of aqueous SDS solutions with and without dispersed alumina nanoparticles was measured using the du Noüy ring method⁹ at 25 °C. The alumina nanoparticles were ultrasonically dispersed in the surfactant solution as described above. Before measurement, the surfactant solution/dispersion was transferred to a clean Petri dish of diameter 60 mm and was allowed to stand for 24 h at 25 °C (inside an air thermostat). The final result is an average of at least three measurements with an error less than 0.2 mN m⁻¹.

(c) Adsorption of surfactant at particle–water interface. The adsorption isotherm of SDS at the alumina particle–water interface from aqueous dispersions was measured by a depletion method at 25 °C. 0.5 wt% alumina nanoparticles were dispersed in aqueous solutions of SDS of different concentration as described above, and the dispersions were allowed to settle for 24 h. Then the surface tension of the dispersion was measured as described above (without separating the particles) and the equilibrium SDS concentration (ccmc) in the dispersion was obtained from the measured surface tension using the surface tension of the SDS solution without alumina particles as calibration. The adsorption of SDS on particles was calculated from the following equation:

\[ \Gamma (\text{mmol g}^{-1}) = \frac{V(C_0 - C_e)}{m} \]  

(1)

where \(C_0\) and \(C_e\) (mol L⁻¹) are the initial and equilibrium concentrations of SDS in the dispersion, respectively, \(V\) (mL) is the volume of the solution and \(m\) (g) is the mass of particles.

(d) Concentration of alumina nanoparticles in aqueous phase of emulsions. A certain mass of alumina nanoparticles was weighed into a bottle of 40 mL (2.7 cm (d) × 9.5 cm (h)), followed by addition of 15 mL of aqueous SDS solution of different concentrations. The particles were dispersed for 1 min using an ultrasonic probe. 15 mL of n-decane was then added and the mixture was emulsified using the homogenizer as described above. The vessels were securely closed using screwed rubber caps and the emulsions were placed upside-down in a thermostated container at 25 °C for 24 h to allow creaming. Then the resolved aqueous phase was withdrawn using a syringe and transferred to a weighed glass bottle of 25 mL. The mass of aqueous phase was recorded. Water was evaporated by heating close to 100 °C in an oven and the particles were finally dried at 110 °C until constant weight. The weight of the particles was recorded from which the concentration (mass percentage) of alumina nanoparticles dispersed in the aqueous phase of the emulsion can be calculated.

Unless specified otherwise, all experiments were carried out at 20–25 °C.

3. Results and discussion

3.1 Pickering emulsions stabilized by alumina nanoparticles plus SDS

Alumina nanoparticles are positively charged at acidic and neutral pH and negatively charged at alkaline pH. The isoelectric point of the particles was measured to be 10.6, as shown in Fig. S3,† a little higher than that reported in the literature of 9.5.⁵²,⁵³ This means that the particles are positively charged in pure water (pH = 6.1). Although the particles have a primary diameter of 13 nm according to the supplier and the TEM image, they aggregate to some extent to give an average particle...
diameter of around 190 nm and a polydispersity of 0.12 at concentrations between 0.01 wt% and 0.1 wt% when dispersed ultrasonically in pure water (measured by light scattering, Fig. S4†).

In pure water, the alumina nanoparticles are therefore highly hydrophilic and surface-inactive, as evidenced by Fig. 1(A) where the particles alone do not stabilize an emulsion at particle concentrations between 0.1 and 1.0 wt%. Particles prefer to remain dispersed in the aqueous phase and exhibit partial sedimentation. The anionic surfactant SDS alone does not stabilize an n-decane-in-water emulsion either at concentrations below 0.6 mM (ca. 0.1 cmc), as shown in Fig. 1(B). However, when 0.5 wt% alumina nanoparticles co-exist with a trace amount of SDS (<0.6 mM), stable n-decane-in-water emulsions are formed as shown in Fig. 1(C), where creaming occurs soon after preparation but coalescence was not observed 24 h after homogenization. The appearance of the emulsion remained almost unchanged a month later except that some sedimentation of particles in the aqueous phase occurred as shown in Fig. 1(D). The extent of sedimentation decreased with increasing surfactant concentration until none was evidenced above 0.3 mM SDS. The micrographs shown in Fig. 2(a−f) indicate that the droplet size of the emulsions decreases with increasing SDS concentration, but the droplets are in general larger than >50 μm, in contrast to those in emulsions stabilized by SDS alone at high concentration which are <50 μm as shown in Fig. 2(g−i). The larger droplet size of Pickering emulsions compared with conventional emulsions has been observed in systems stabilized by silica nanoparticles in combination with a trace amount of cationic surfactant5,39,44 or zwitterionic surfactant at low pH.47 We thus believe emulsions stabilised by alumina nanoparticles and a trace amount of SDS are also Pickering emulsions. This can be further evidenced by the micrographs of oil droplets shown in Fig. 3, where the n-decane

![Micrographs of n-decane-in-water emulsions stabilized by 0.5 wt% alumina nanoparticles in combination with SDS at different concentrations (a−f), and stabilized by SDS alone at different concentrations (g−i), taken 24 h after preparation. [SDS] for (a) to (f): 0.01, 0.02, 0.03, 0.06, 0.1 and 0.2 mM and for (g) to (i): 0.6, 1.0 and 2.0 mM.](image)

![Micrographs of n-hexane-in-water emulsion droplets (a) half-dried and (b) fully dried stabilized by 0.5 wt% alumina nanoparticles in combination with 0.1 mM SDS, taken 20 min (half-dried) and 30 min (fully dried), respectively, after placing a drop of emulsion on a glass slide.](image)
has been replaced by a more volatile oil n-hexane and the emulsion is allowed to evaporate. After some time, a wrinkled skin or particle shell can be seen on the surface of the droplet (a), whereas after further time clear patches of solid film were observed (b). These features are characteristic of Pickering emulsions stabilised by particles alone\(^5-^4\) and did not appear in emulsions of SDS alone.

### 3.2 Demulsification/re-stabilization of Pickering emulsions

The Pickering emulsions have very good long term stability to coalescence, which however poses a difficulty for demulsification. In cases where the particulate emulsifiers are inorganic nanoparticles hydrophobized in situ by suitable amphiphiles, demulsification can be achieved easily by removing the in situ hydrophobization. For example, the hydrophobization of silica nanoparticles by cationic surfactants can be removed by either switching off the cationic surfactant to its uncharged form\(^5,^4,^5\) or by addition of an oppositely charged anionic surfactant which prefers to form ion pairs with it resulting in desorption of the cationic surfactant from particle surfaces.\(^4,^5\) For the Pickering emulsion stabilized by alumina nanoparticles hydrophobized in situ by SDS, addition of a cationic surfactant should be effective but in order to re-stabilize the emulsion additional SDS should be added. However, the accumulation of both surfactants in the system may finally negate the stimuli-responsiveness of the system in multiple cycles. Here we use a switchable surfactant DDAA, which can be transformed between amidinium/cationic and amidine/neutral forms by bubbling CO\(_2\) and N\(_2\) into water\(^5\) as shown in eqn (2) to introduce the CO\(_2/N_2\) trigger to the system. An otherwise stable Pickering emulsion containing 0.5 wt% alumina nanoparticles and 0.3 mM SDS was initially prepared in the container of a glass bubbling device shown in Fig. S2.\(^\dagger\) This is composed of a column container and a bubbling tube together with an air distributor where the upper side of the bubbling tube can be connected to a condenser to reduce the evaporation loss of liquid during bubbling at elevated temperature. Then DDAA in amidinium/cationic form of equal moles to the SDS in the emulsion was added into the stable Pickering emulsion as a concentrated aqueous solution (30 mM) and demulsification ensued. The demulsified mixture was then bubbled with N\(_2\) at 65 °C and re-homogenised followed by bubbling the emulsion with CO\(_2\) at 0–5 °C alternately to trigger multiple demulsification/re-stabilization events, as shown in Fig. 4.

\[
\begin{align*}
\text{C}_{12}\text{H}_{25}-\text{N}^+ & \text{N}^- \text{CH}_3 & \text{C}_{12}\text{H}_{25}-\text{N}^- \text{H}^- \text{CH}_3 \\
\text{CH}_3 & \text{CO}_2, \text{0-5°C} & \text{HCO}_3^- \\
\text{N}_2/\text{air, 65°C} & & \text{amidine/neutral} \\
& & \text{amidinium/cationic}
\end{align*}
\]

It is seen from Fig. 4 that the initial stable Pickering emulsion (A) has an average droplet diameter of ca. 50 μm as shown in micrograph (a), and demulsification occurs when DDAA in the amidinium/cationic form is added to the emulsion with gentle mixing (B). The re-stabilization of the emulsion can be achieved by bubbling N\(_2\) into the system for 80 min at 65 °C followed by homogenization (C). The droplet size of the re-homogenized emulsion (e) is only slightly larger than that of the original emulsion. Demulsification of this stable Pickering emulsion can be achieved by bubbling CO\(_2\) into the emulsion for 80 min at 0–5 °C (D) where a small volume of oil and water (0.7 mL each) is added to compensate the slight evaporation during bubbling at elevated temperature. The re-stabilization/demulsification steps can be cycled by bubbling N\(_2\) and CO\(_2\) alternately (E and F) and a similar droplet size can be reached for the stable emulsion (e). Although in principle the demulsification/emulsification transformation can be cycled many times, it is found that the demulsification efficiency is reduced with increasing cycle number. This is because the switching on of DDAA surfactant is not complete by bubbling CO\(_2\) (ref. 5) and hydrolysis of DDAA is possible at elevated temperature. The extent of hydrolysis of 10.1% during a demulsification/emulsification cycle was roughly estimated by measuring the concentration of DDAA remaining in aqueous solution after bubbling N\(_2\) at 65 °C for 3 h followed by bubbling CO\(_2\) at 0–5 °C for another 3 h for a DDAA solution at an initial concentration of 13.5 mM using HPLC-MS. The cationic amidinium available in the emulsion thus decreases gradually with time resulting in incomplete demulsification. This problem can be solved however by addition of more DDAA into the system since DDAA in either form does not interact with alumina particles and therefore demulsification/emulsification is not affected. In this way switchable Pickering emulsions triggered by CO\(_2/N_2\) are obtained.

### 3.3 Probing into the mechanism

As previously reported\(^3,^4,^5,^6,^7\) charged inorganic nanoparticles can be hydrophobized in situ by adsorption of oppositely charged surfactant via electrostatic interaction in water. The alumina nanoparticles are positively charged as evidenced by the zeta potential of +40.8 mV when dispersed in pure water (pH of dispersion = 5.85) as shown in Fig. S3\(^\dagger\) and can therefore be hydrophobized by adsorption of anionic surfactant SDS. In fact

\[
\text{C}_{12}\text{H}_{25}-\text{N}^+ \text{N}^- \text{CH}_3 \quad \text{CO}_2, \text{0-5°C} \quad \text{C}_{12}\text{H}_{25}-\text{N}^- \text{H}^- \text{CH}_3 \quad \text{HCO}_3^- \\
\text{N}_2/\text{air, 65°C} \quad \text{amidine/neutral} \quad \text{amidinium/cationic}
\]
the hydrophobization of alumina particles by negatively charged short amphiphiles and functional polymer has been reported.

The adsorption of SDS at the alumina particle–water interface can be assessed by measuring the adsorption isotherm of the surfactant as well as the zeta potential of the particles dispersed in aqueous SDS solutions. Fig. 5 shows the adsorption isotherm at 25 °C obtained via surface tension measurements shown in Fig. 6. The surface tension of the solutions increases on addition of alumina particles, indicating a decrease of the surfactant concentration in the aqueous phase due to adsorption by the particles. It was found that the surface tension (γ) of aqueous SDS solutions without particles as a function of SDS concentration (C) can be well fitted by the Szyszkowski equation, \( \gamma = \gamma^0 - 2RT \ln(1 + KC) \) with \( \gamma^0 = 3.27 \times 10^{-19} \) mol cm\(^{-2}\) and \( K = 1.33 \times 10^5 \) L mol\(^{-1}\), where \( \gamma^0 \) is the surface tension of pure water, \( R \) is the gas constant, \( T \) is the absolute temperature, \( K \) is a constant reflecting adsorption free energy and \( \gamma^0 \) is the saturated adsorbed amount. The equilibrium concentration (\( C_e \)) of SDS in the dispersion can then be calculated directly based on the measured surface tension of the dispersion. It is found that the adsorption of SDS on particle surfaces increases with an increase in the equilibrium surfactant concentration. At low concentration (ca. below 0.5 mM) monolayer adsorption occurs via electrostatic interaction between the negative charge of SDS and positive charge on particle surfaces rendering particles partially hydrophobic. For example, at an initial concentration of 0.3 mM (equilibrium concentration = 0.028 mM where SDS alone cannot stabilize an emulsion), the adsorbed amount of SDS is around 0.054 mmol g\(^{-1}\) equivalent to a cross-sectional area per SDS molecule of 3.08 nm\(^2\), which is much higher than that of SDS at the air–water interface (0.52 nm\(^2\) per molec.\(^{-1}\)) at saturated adsorption, suggesting monolayer adsorption. Upon increasing further the SDS concentration, double layer or hemi-micelle adsorption occurs via chain–chain interactions between SDS molecules rendering particles hydrophilic again. As an example, at an equilibrium
concentration of 5.4 mM (close to cmc = 6.2 mM, Fig. 6), the adsorption reaches 0.921 mmol g\(^{-1}\), corresponding to a cross-sectional area of 0.18 nm\(^2\) per molec. (< 0.52 nm\(^2\) per molec.).

In accordance with the adsorption of SDS on particle surfaces, the zeta potential of alumina particles dispersed in aqueous SDS solutions decreases with increasing SDS concentration, as shown in Fig. 7 (filled circles). The inherent positive charges on particle surfaces are neutralized by the negatively charged surfactant. Particles exhibiting a zeta potential around zero were formed at an initial SDS concentration of ca. 0.5 mM, where the adsorption of SDS reaches 0.07 mmol g\(^{-1}\) corresponding to a cross-sectional area of 2.37 nm\(^2\) per molecule (monolayer adsorption). The zero zeta potential is supported by the flocculation of the particles (0.1 wt%) dispersed in 0.3 mM SDS as shown in Fig. S4† where the average particle size increases from ca. 190 nm in pure water to nearly 600 nm and the polydispersity increases from 0.135 to 0.301. At higher SDS concentrations, the zeta potential of the particles becomes negative as a result of double layer or hemi-micelle adsorption of SDS molecules. It is believed the SDS molecules initially adsorb on particle surfaces with a head-on configuration driven by electrostatic attraction. The formation of a monolayer reduces the hydrophobicity of the particles and endows them with sufficient surface activity enabling their adsorption at the oil–water interface in stabilizing emulsions. In the previous section we provided micrographs (Fig. 3) which clearly show the adsorption of the particles at droplet surfaces. In addition we have determined the amount of particles adsorbed at the oil–water interfaces in emulsions by measuring the concentration of particles which are non-adsorbed in the aqueous phase as shown in Table 1. It is seen that at an initial SDS concentration of 0.01 mM, only 23% of the particles adsorb to the oil–water interfaces. However, this increases to 88% at 0.1 mM SDS and further increases to 97% at 1 mM SDS. In contrast, when SDS is replaced by DDAA in amidinium/cationic form the percentage of particles adsorbed is very low (<5%) and does not change with surfactant concentration. This is because the cationic surfactant does not induce hydrophobization of the alumina nanoparticles being of the same charge sign.

When DDAA in amidinium/cationic form is added to the emulsion stabilized by alumina nanoparticles hydrophobized in situ by SDS, the cationic surfactant tends to form ion pairs with SDS which are not soluble in water and which precipitate from solution at concentrations above 0.06 mM, as shown in Fig. S5.† Desorption of SDS from particle surfaces occurs and alumina particles are rendered hydrophilic again. Particles return to the aqueous phase from emulsion droplet interfaces followed by droplet coalescence and ensuing demulsification. This is evidenced by the fact that the zeta potential of alumina particles dispersed in aqueous solutions of equimolar mixtures of SDS and DDAA (in amidinium/cationic form) is highly positive.

### Table 1

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<thead>
<tr>
<th>Alumina + SDS</th>
<th>Alumina + DDAA</th>
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<tbody>
<tr>
<td><strong>C(_{SDS}/\text{mM})</strong></td>
<td><strong>C(_{p}/\text{wt}%)</strong></td>
</tr>
<tr>
<td>0.01</td>
<td>0.385 ± 0.006</td>
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<tr>
<td>0.1</td>
<td>0.060 ± 0.002</td>
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<tr>
<td>1.0</td>
<td>0.016 ± 0.002</td>
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(Fig. 7) and no stable Pickering emulsion was produced when \( n \)-decane was homogenized with the dispersion, as shown in Fig. 8. When the DDAA surfactant is switched off to the amidine/neutral form by bubbling with \( N_2 \), the ion pairs collapse and the SDS molecules are released. As evidence, the zeta potential of the particles dispersed in equimolar mixtures of SDS/DDAA (in amidinium/cationic form) decreases to close to the values in dispersions with SDS alone following bubbling with \( N_2 \), as shown by the open triangles in Fig. 7. The slightly higher zeta potential values than that in systems of SDS alone may be due to incomplete switching off of the DDAA\(^+\) so that the concentration of free SDS in the system following bubbling with \( N_2 \) is a little lower than that in a dispersion with SDS alone at specified initial concentration. The \textit{in situ} hydrophobization of the alumina particles can then take place again and a stable Pickering emulsion is formed after homogenization.

4. Conclusions

We have demonstrated that switchable Pickering \( n \)-decane-in-water emulsions can be prepared by using positively charged alumina nanoparticles in combination with a trace amount of a conventional anionic surfactant (SDS) and a \( CO_2/N_2 \) switchable surfactant such as DDAA. When the switchable surfactant is switched off to the amidine/neutral form by bubbling with \( N_2 \) at 65 °C, the hydrophilic alumina nanoparticles are hydrophobized \textit{in situ} by adsorption of SDS molecules endowing them with sufficient surface activity to stabilise a Pickering oil-in-water emulsion. On the other hand when the emulsion was bubbled with \( CO_2 \) at low temperature, DDAA is switched to the amidinium/cationic form and prefers to form ion pairs with SDS molecules. The \textit{in situ} hydrophobization is removed due to desorption of SDS molecules from particle surfaces resulting in demulsification of the emulsion. The emulsification/demulsification cycle can be repeated several times. This protocol is applicable to other positively charged colloid particles in preparing switchable Pickering emulsions.

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