CO₂/N₂ Responsive Pickering Emulsion Stabilized by Silica Nanoparticles and a Common Nonionic Surfactant

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Abstract. Responsive emulsions with controllable stability are of growing interests in recent years. These emulsions are usually stabilized by specially synthesized surfactants, polymers, solid particles or their mixtures with switchable functional groups. However, these emulsifiers are inconvenient for extensive utilizations due to their complicated synthesis processes. Here we propose a new approach of using hydrophilic silica nanoparticles activated by a conventional polyoxyethylene nonionic surfactant to prepare responsive Pickering emulsions triggered by CO₂/N₂. The addition or removal of CO₂ is to simply change the amount of silanols on the particle surface, increasing or decreasing the adsorbing sites for hydrogen bonding with oxyethylene groups. The adsorption amount of the polyoxyethylene nonionic surfactant onto silica nanoparticles can be significantly increased when CO₂ is introduced, making the particles hydrophobized in situ and become excellent stabilizers for Pickering emulsions. While N₂ was bubbled at an elevated temperature to remove the dissolved CO₂, the substantial desorption of the surfactant from the particle surface can make silica nanoparticles regain their hydrophilic nature, and therefore emulsions stabilized by such particles can be broken.

1. Introduction

Interests in responsive emulsions that can be transformed between stable and unstable states have been growing over the past few years[1]-[5]. The controllable stability of these emulsions depends mainly on the stimuli-responsive performance of the utilized emulsifiers between active and inactive forms via appropriate triggers. A variety of responsive emulsifiers have been developed, including surfactants, polymers and colloidal particles sensitive to pH[6], carbon dioxide (CO₂)[7], temperature[8], light[9], magnetism[10], and other triggers[11]. Among those CO₂ is a unique and attractive one as it is widely available, inexpensive, environmentally benign, and easy to apply. While bubbled into an aqueous solution, dissolved CO₂ coexists with carbonic acid in balance. The increase in acidity, i.e. the grow in number of H⁺, facilitates certain chemical moieties including amidine, guanidine, amine, carboxyl and so on to undergo ionic or conformational changes, altering the solubility, surface activity, and wettability of the emulsifiers[12]. The dissolved CO₂ can be easily removed from the solution by bubbling another gas, such as N₂, Ar, or air, at ambient or elevated temperature. Superior to pH adjustment by acid and alkali, the introduction and removal of CO₂ is a non-accumulative process, and thus the variation of electrolyte concentration can be negligible.

Jessop and co-workers have reported a type of responsive surfactant triggered by CO₂/N₂, wherein the alkyl amidine (N'-dodecyl-N,N-dimethylacetamidine) can be protonated to become a cationic oil-in-water emulsifier upon the introduction of CO₂ into the aqueous solution, and then be deprotonated...
to regain its surface inactive form by bubbling N$_2$. Jiang and Zhu have transferred the CO$_2$/N$_2$ stimuli response of the switchable surfactant to silica nanoparticles through in situ hydrophobization in aqueous phase, and this strategy allows for the formation of CO$_2$ responsive Pickering emulsions and foams using only a trace amount (0.1-0.5 cmc) of the switchable surfactant. Liang et al. grafted silica nanoparticles with CO$_2$ switchable functional groups and hydrophobic functional groups to prepare surfactant-free CO$_2$ responsive emulsions. Based on the surface wettability variation of the modified particles, emulsification and demulsification took place circularly upon the cycling treatments of air and CO$_2$. Nevertheless, the above emulsifiers containing certain CO$_2$ sensitive functional groups in active form are now limited to cationic types. Moreover, their synthesis or preparation is quite complicated, making these emulsifiers inconvenient for extensive applications.

Herein, we describe a new idea that uses silica nanoparticles combined with a conventional polyoxyethylene nonionic surfactant to prepare CO$_2$ responsive Pickering emulsions. In contrast to most of the previous studies, the addition of CO$_2$ is not for changing the surfactant from inactive (neutral) to active (cationic) form. Instead, its purpose is to simply increase the number of silanols on the surfaces of nanoparticles, offering more adsorbing sites for hydrogen bonding with oxyethylene groups[13]-[15]. The adsorption amount of the polyoxyethylene nonionic surfactant onto silica nanoparticles is significantly increased with the addition of CO$_2$, making the particles hydrophobized in situ and become excellent Pickering emulsion stabilizers. While N$_2$ was bubbled at an elevated temperature to remove the dissolved CO$_2$, the number of silanols on the particle surface is reduced due to deprotonation and therefore the adsorbing sites between particles and surfactant molecules become less, leading to the substantial desorption of surfactant from the particle surface. As a result, silica nanoparticles regain their hydrophilic nature and emulsions stabilized by such particles are thus destabilized.

2. Experimental Section

2.1. Materials

Commercial colloidal silica nanoparticles, Ludox HS30, were purchased from Grace Chemicals. These nanoparticles were received as an aqueous dispersion at a solid concentration of 30wt%. These particles are spherical and relatively monodisperse with an average diameter of approximately 15nm. Nonaethylene glycol monododecyl ether (C$_{12}$E$_9$) was used as the typical nonionic surfactant in this study. It was a gift from Lantian Finechem Company with a purity of 98%. Liquid paraffin (chemical purity) was purchased from Sinopharm and treated with activated carbon for 3 times to remove polar impurities prior to use. High purity CO$_2$ and N$_2$ were provided by Qingdao Tianyuan Gas Manufacturing Company. Ultrapure water was produced by a Milli-Q reagent water system. Its electrical resistivity and surface tension at 25°C are respectively 18.25MΩ·cm and 72.18mN·m$^{-1}$.

2.2. Experimental Methods

2.2.1. Measurement of contact angle. Planar quartz plates (3cm×2cm) were used as model silica substrates for contact angle measurements. These plates were treated with chromic acid and rinsed with distilled water before use to make them hydrophilic. Contact angle of a captive liquid paraffin drop in aqueous solution on a quartz surface was determined by the DSA100 drop shape analyzer instrument at 25°C. For each measurement, a quartz plate was equilibrated in the aqueous surfactant solution in the glass cell for 24hrs, and then a drop of liquid paraffin was released from the bottom and captured by the lower surface of the plate. After 10mins for equilibrium, the contact angle through water phase was obtained.

2.2.2. Preparation and switching of emulsions. Equal volumes of aqueous dispersion and liquid paraffin were added to a glass vessel and then were homogenized at 10000rpm for 2mins with a high-speed homogenizer (IKA T18, Germany). Immediately after preparation, the emulsion type was
determined via a drop test, and then the prepared emulsion was loaded into a sealed sample bottle for further observation. The emulsion stability to coalescence and creaming was evaluated by monitoring the phase separation within 15 days at 25°C. For the stimuli responsivity test, an emulsion prepared by the nanoparticle-surfactant mixture in the inactive form was bubbled with CO₂ at a flowrate of 150mL·min⁻¹ for 30 mins at 25°C followed by homogenization, so as to identify the switching on performance. Then for the switching off experiment, this stable emulsion was bubbled with N₂ at the same flowrate for 50 mins at 65°C (water bath) followed by rehomogenization, and the destabilization of the emulsion was observed. The switching on and off process was repeated for several circles.

3. Results and Discussion

3.1. Contact angle of silica surface in the presence of C₁₂E₉

To identify the influence of surfactant adsorption on the hydrophobicity of nanoparticles, we measured the contact angle variation using quartz as a substitution. As shown in Figure 1, in the case that surfactant solutions were not treated by CO₂, the contact angle increased monotonically with the increasing surfactant concentration, and finally reached 27° at 0.2 mM C₁₂E₉. While surfactant solutions had been bubbled with CO₂, the contact angle increased with the increasing C₁₂E₉ concentration up to 0.1 mM and then decreased at higher concentrations, with the largest contact angle being 42.5° at 0.1 mM C₁₂E₉. The increase in hydrophobicity results from the oxyethylene head groups interacting with the silanols on the quartz surface through hydrogen bonding, whereas the hydrophobic chains of the surfactant molecules extend into the liquid phase.¹⁵⁻¹⁷ The difference between the hydrophobic degrees in the two cases with and without CO₂ treatment is ascribed to the different adsorbed amounts as mentioned before. Besides, the decrease in contact angle at high C₁₂E₉ concentrations in the case that CO₂ treatment was applied may be caused by the double layer or semimicelle adsorption of the surfactant.

![Fig.1. Contact angle of liquid paraffin drop on quartz plate in aqueous C₁₂E₉ solutions with and without dissolved CO₂ as a function of surfactant concentration.](image-url)
3.2. Characterization of Pickering Emulsions

Silica nanoparticles alone were too hydrophilic to stabilize Pickering emulsions. Also, emulsions stabilized by the nonionic surfactant C$_{12}$E$_9$ at concentrations lower than cmc were fragile. When silica nanoparticles and C$_{12}$E$_9$ worked together without CO$_2$ treatment, phase separations were also observed 24hrs after preparation at surfactant concentrations lower than 0.08mM (Figure 2a). In this case the stability of emulsions was not improved, indicating that the nonionic surfactant and nanoparticles showed nearly no synergistic effect. This is consistent with the above findings in Figure 1, which demonstrates that the silica nanoparticles remained hydrophilic and inactive due to the very low adsorption amount of surfactant on the particle surface. However, when dispersions of 0.5wt% nanoparticles and a trace amount of C$_{12}$E$_9$ (as low as 0.008mM, ≈0.08cmc) were bubbled with CO$_2$, the strong adsorption of surfactant led to the in situ hydrophobization of particles, giving them good ability to stabilize emulsions. Figure 2(b and c) show that although creaming occurred, these emulsions were completely stable to coalescence at C$_{12}$E$_9$ concentrations between 0.008 and 0.1mM within the study period.

![Fig. 2. Photographs of liquid paraffin-in-water emulsions stabilized by 0.5wt% silica nanoparticles in combination with different concentrations of C$_{12}$E$_9$ without (a) and with (b and c) CO$_2$ treatment. Pictures were taken respectively 24hrs (a and b) and 15days (c) after preparation. The concentrations of surfactant from left to right are 0.001, 0.005, 0.008, 0.01, 0.05, 0.08, 0.1 mM, respectively.](image-url)
3.3. Switching test of Pickering emulsions
The transformation of the emulsion between stable and unstable forms was tested. Firstly, an oil-in-water emulsion was prepared by homogenization equal volumes of liquid paraffin and aqueous dispersion containing 0.5wt% nanoparticles and 0.05mM C$_{12}$E$_9$. As the nanoparticle-surfactant mixture had not been activated, complete phase separation occurred after placed for 24hrs (Figure 3a). Then the switching on examination was conducted by bubbling CO$_2$ followed by rehomogenization. Although creamed, the generated emulsion didn’t coalesce within the standing period of 15days (Figure 3b), indicating that the emulsion had been switched from unstable to very stable form. For the switching off test, N$_2$ was bubbled into the stable emulsion to eliminate the dissolved CO$_2$. It was observed that oil was released continuously during the bubbling process, and finally the two phases separated completely (Figure 3c). Rehomogenization was carried out to confirm that the emulsion was broken by making silica nanoparticles lose their surface activity rather than the simple gas bubbling. The phase behaviors at different times after homogenization are shown in Figure 3(d and e). After placing for 1hr, a coarse emulsion with a quite light color was observed (Figure 3d), indicating that the emulsion was undergoing a coalescence process. The unstable emulsion then separated into two phases completely 24hrs later (Figure 3e). Based on the fact that stable emulsions could not be regenerated, we can identify that the demulsification was caused by the inactivation of nanoparticles. Through bubbling CO$_2$ and homogenizing for another time, the stable emulsion was generated again (Figure 3f). The switching on and off processes were repeated for several more cycles, and the cycle number seemed to have no influence on the stability of the emulsion (not shown here).

4. Conclusions
Responsive Pickering emulsions can be prepared using hydrophilic silica nanoparticles combined with a trace amount of a conventional nonionic surfactant (nonaethylene glycol monododecyl ether, C$_{12}$E$_9$). Upon bubbling CO$_2$ the number of silanols on the surface of silica nanoparticles is increased, which offers more adsorbing sites for the polyoxyethylene nonionic surfactant, making the particles hydrophobized in situ and become excellent emulsifiers. While N$_2$ was bubbled at an elevated temperature to remove the dissolved CO$_2$, the adsorbing sites between particles and surfactant molecules are eliminated and thus the silica nanoparticles regain their hydrophilic nature, leading to the destabilization of emulsions. The switching on and off process can be easily repeated. Compared with the emulsions stabilized by specially synthesized surfactants, polymers, colloidal particles or their mixtures, the new approach proposed here is simpler and more convenient as the complicated
synthesis processes are avoided. The silica nanoparticles and the nonionic surfactant used here are both commercially available and commonly used ones. In addition, we believe that this method may be applicable for other kinds of particles whose surface silanols can be altered, such as alumina oxide and titanium oxide, and also other nonionic surfactants containing polyoxylethylene groups.

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