Competition Between Hydrogen Bonding and Electrostatic Repulsion in pH-Switchable Emulsions

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Keywords. Pickering emulsions; oil-in-dispersion emulsions; adsorption; escin; nanoparticles

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ABSTRACT

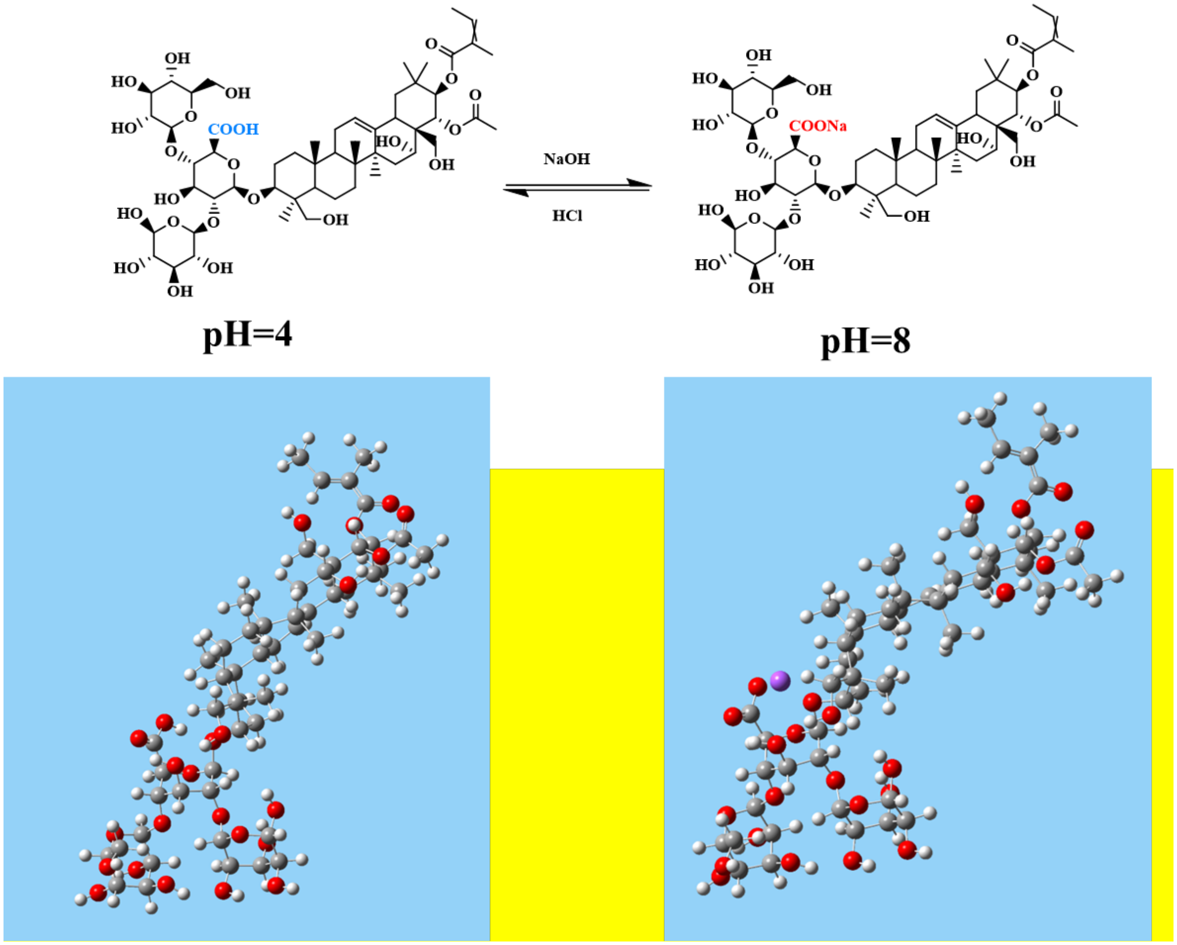
Electrostatic interactions and hydrogen bonding play important roles in the stabilization of self-assembled systems. However, the competition between hydrogen bonding and electrostatic repulsion in emulsions hasn't been reported. Herein, we report on electrostatic repulsion overcoming hydrogen bonding in oil-in-water (O/W) emulsions prepared by the mixture of escin and hydrophilic silica nanoparticles triggered by pH, in which the location of the nanoparticles is reversibly transformed from being adsorbed at oil-water interface to dispersion in the continuous phase. Escin adsorbs on silica particles in alkaline solution by its hydroxyl groups to endow the particles with surface activity, yielding a stable Pickering emulsion. However, such adsorption *via* hydrogen bonding is reversed by electrostatic repulsion between carboxylate ions and negatively charged silica particles after escin was converted to sodium aescinate. Demulsification occurred after silica particles reverted to being hydrophilic, which could further co-stabilize the oil-in-dispersion (OID) emulsions with sodium aescinate through electrostatic repulsions after re-homogenization. Pickering or OID emulsions with high internal phase volume fraction could also be obtained. This strategy is universal for O/W emulsions stabilized by nanoparticles and similarly charged surfactants with a polar headgroup near the nonionic functional group, *e.g.* silica plus polyoxyethylene lauryl ether carboxylate. This work aids in understanding the role of electrostatic repulsion and hydrogen bonding in stabilizing emulsions and sheds light on the design of smart surfactants for practical applications.

1. Introduction

Hydrogen bonding is non-covalent in nature and is widely involved in self-assembled systems, such as supramolecular solutions, hydrogels and emulsions.[1,2] As an example, Pickering emulsions can be stabilized by nonionic surfactant-coated nanoparticles through the adsorption of surfactant *via* hydrogen bonding [3]. On the other hand, electrostatic interactions also have a great impact on the stabilization of Pickering emulsions. For example, ionic surfactants can adsorb on oppositely charged particle surfaces through electrostatic attraction to endow particles with surface activity. [4,5] Recently, Weinhold and Klein [6] and Strate *et al.*[7] reported that hydrogen bonding can overcome like-charge electrostatic repulsion in ionic liquids.[8] However, the competition between electrostatic repulsion and hydrogen bonding in emulsions has been less studied.

Pickering emulsions are always more stable than conventional emulsions, [9-16] which are suitable therefore for long-term storage as required in the food and cosmetics fields. [9-11] However, the properties of Pickering emulsion such as high viscosity and difficulty in demulsification constitute an obstacle in applications requiring temporary stability, such as in biphasic catalysis or emulsion polymerization. [17-20] In recent decades, switchable (stimuli-responsive) Pickering emulsions have been developed, [21,22] in which stable and unstable emulsions can be controlled by various triggers such as CO_2/N_2, redox, light irradiation, pH, magnetic field and temperature. [23-32] For example, Pickering emulsions stabilized by nonionic surfactant-coated silica particles are thermo-responsive, in which the hydrogen bonding between the surfactant and particles is partly destroyed at high temperature. [32] However, increasing temperature in large-scale applications is time and energy consuming. In addition, although the above switchable methods endow Pickering emulsions with controllable stability, variable viscosity of emulsions is still not easily achievable [33] which is crucial in many applications including oil transportation and cutting fluids. [34]

Recently, mixtures of like charged nanoparticles and surfactant were reported to stabilize oil-in-dispersion (OID) emulsions, [35] in which particle-droplet and particle-particle electrostatic repulsions are important for their stability. [35-38] Despite similar viscosity and droplet size to conventional emulsions stabilized by surfactant, OID emulsions have much lower stability than that of Pickering emulsions. Herein, we report on O/W emulsions co-stabilized by a biosurfactant (escin, Scheme 1) and hydrophilic silica particles in which the competition between electrostatic repulsion and hydrogen bonding can be triggered by pH. In acidic and neutral media, uncharged escin adsorbs on silica particles *via* hydrogen bonding endowing them with surface activity to stabilize Pickering emulsions. In alkaline media however, escin is converted to anionic sodium aescinate (abbreviated as SA) and the hydrogen bonding is weakened or eliminated due to the electrostatic repulsion between SA and negatively charged particles, which favors the formation of OID emulsions. As a result, reversible conversion between Pickering and OID emulsions can be achieved under specific pH conditions, and the properties of emulsions such as stability, droplet size and viscosity can be controlled by the pH trigger.



Scheme 1. Chemical structure of (left) escin and (right) sodium aescinate and their pH response in water. Red spheres represent hydroxyl groups and the violet sphere at pH = 8 represents the COO^- group.

2. Experimental

2.1 Materials

Silica nanoparticles (primary particle diameter = 20 nm) with a purity > 99.8% were purchased from Wuxi Jinding Longhua Chemical Co. Ltd. (China). Escin (> 95%) was obtained from Sigma. *n*-octane was purchased from TCI. [3-(diethylamino) propyl] trimethoxysilane or KH792 (> 95%)

was purchased from Adamas. Citric acid (> 99.5%) was purchased from Sinopharm Chemical Reagent Co. Ltd. $C_{12}E_3$ (>99%), polyoxyethylene lauryl ether carboxylate (abbreviated as LCA-3, > 99%) and 13-polyether (3) tridecanoic acid (abbreviated as PTDA, > 98%) were received from Haian Petrochemical Plant. Ultrapure water (18.2 MΩ cm, pH = 6.1 at 25 °C) used in all experiments was produced from a Simplicity Pure Water System (Merck Millipore, Shanghai).

2.2 Preparation and characterization of emulsions

Silica nanoparticles (0.1 wt.%) were dispersed in 7 cm^3 aliquots of escin solution or pure water (pH = 7) using an ultrasonic probe and then equal volumes of octane were added to prepare emulsions followed by homogenization using an Ultra-turrax homogenizer (8000 rpm, 2 min). The type of emulsion was determined by the drop test and by staining. Nile red was used to color the oil. Optical micrographs of emulsions were recorded using a VHX-1000 microscope system (Keyence Co.). A small volume of emulsion was placed on a clean polished silicon wafer at 25 °C to allow water and oil to evaporate completely. SEM images were recorded using a scanning electron microscope (Hitachi Corporation, S-4800).

2.3 Adsorption of escin/SA at silica-water interface

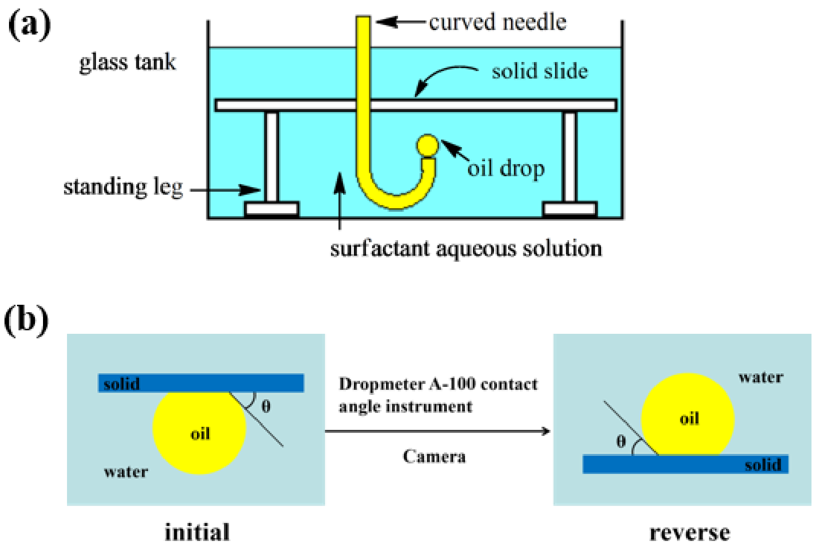
The adsorption isotherm of surfactant (escin/SA) at the silica particle-water interface was measured by a depletion method. Silica nanoparticles (0.1 wt.%) were dispersed in aqueous surfactant solutions of different concentration for 24 h at 25 °C to reach equilibrium. The surface tension of the dispersion was then measured by the du Noüy ring method. The equilibrium concentration of surfactant was calculated from the surface tension of the solution without silica particles as calibration. For a dispersion with an initial surfactant concentration C_0 (mol/L), the equilibrium surfactant concentration (C) can be found from the calibration curve or the concentration of a solution which gives the same surface tension as the dispersion can be determined. The adsorbed amount (mmol/g) of surfactant on the particles was then obtained from:

$$\Gamma = \frac{V(C_0 - C)}{m} \qquad (1\text{-}1)$$

where V is the volume of surfactant solution (mL) and m is the mass of the particles (g).

2.4. Contact angles

The oil-water-glass contact angles were measured by the Dropmeter A-100 contact angle instrument (Maist measurement Co. Ltd., China) through the inverted sessile drop method where an octane droplet (0.5 μL) was first released through a U-shaped needle into the aqueous solution and then captured by the underside of the glass slide (Scheme 2). The glass slide had been immersed in aqueous solutions of different surfactant concentration.



Scheme 2. (a) Schematic of instrument for used for measuring contact angles. (b) Schematic of the side view of an inverted sessile drop.

2.5 Fluorescence labelling of silica

2 g of silica particles were dispersed in 250 mL of pure water. Citric acid (1.759 g) and 35 mL of [3-(diethylamino) propyl] trimethoxysilane were dissolved in 500 mL pure water and stirred for 2 min. The silica particle dispersion was added to the above mixed solution and transferred to a polytetrafluoroethylene autoclave, which was then put in a vacuum oven at 180 ºC for 3 h. After cooling to room temperature, the dried particles were washed with pure water and ethanol three times. The particles emit green light and the fluorescence peak appears at 450 nm.

3. Results and discussion

3.1 Pickering emulsions stabilized by escin-coated silica particles at pH = 4

Escin is a natural nonionic surfactant obtained from a variety of plant species used in the food, cosmetics, medical and other fields (Scheme 1), which contains a rigid hydrophobic tricyclic pentiterpene group and hydrophilic saccharide groups containing hydroxyl and carboxylic acid moieties. [39-42] With a $pK_a = 4.7$ due to the carboxylic acid group,[42] escin is pH responsive and can be reversibly transformed between the nonionic form (escin) and the anionic form (SA). Such a structure conversion of escin was confirmed by ^{1}H-NMR measurements (Figure S1), in which the peaks of the carboxylic acid group (11.6 ppm) disappeared after adding an equimolar amount of NaOH. Similar to studies in the literature,[39,40] the critical micelle concentration (cmc) of escin changed from 6.4×10^{-2} mM (γ_{cmc}= 45.0 mN/m) at pH = 4 to 6.2×10^{-2} mM (γ_{cmc}= 54.3 mN/m) at pH = 8 (Figure S2 and Table S1). The changes in the surface tension after adding NaOH reflect the different arrangement of surfactant molecules at the air-water interface, [39,40] in response to the gradual conversion from nonionic escin (0.42 nm^2/molec.) to anionic SA (0.65 nm^2/molec.).

Conventional O/W emulsions with octane were stabilized by escin alone beyond a concentration of 0.03 mM at pH = 4 (Figure S3), but at lower concentrations emulsions were completely demulsified within 12 h. However, after addition of silica nanoparticles (0.5 wt.%, primary diameter = 20 nm, Figure S4), Pickering emulsions were formed at a very low escin concentration (0.001 mM, 0.0033 cmc) as shown in Figure 1. The emulsions dispersed well in water and green spherical oil droplets could be observed in the stained emulsions (Figure 2a), indicating O/W type. The average droplet diameter decreased from around 200-250 μm to 30-80 μm upon increasing the escin concentration as shown in Figure 1c. The wrinkled particle film morphology of the dried emulsion suggested the accumulation of silica particles on droplet surfaces, confirming the formation of Pickering emulsions (Figure 2c). [13]

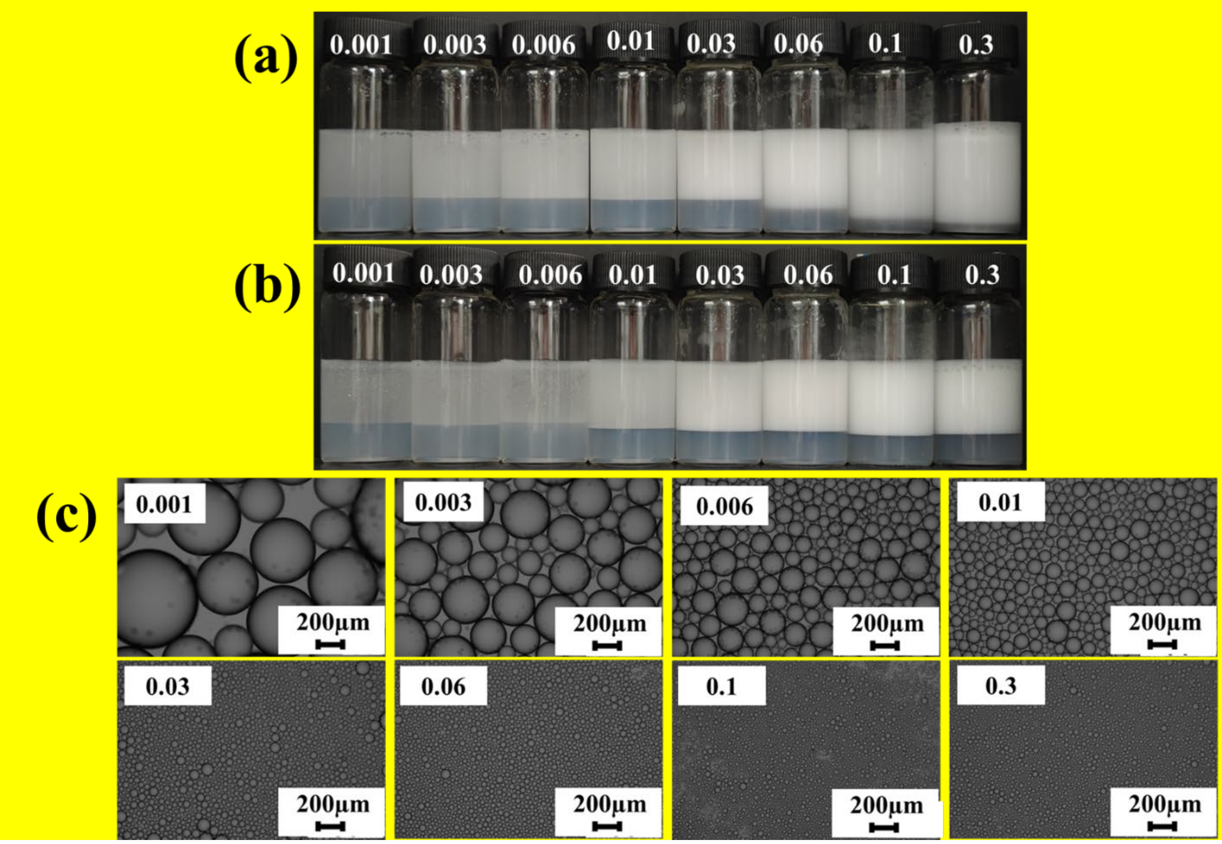


Figure 1. (a, b) Appearance and (c) selected micrographs of *n*-octane-in-water Pickering emulsions stabilized by 0.5 wt.% silica nanoparticles and different concentrations of escin (in mM) at pH = 4 taken (a) immediately, (b, c) 24 h after homogenization.

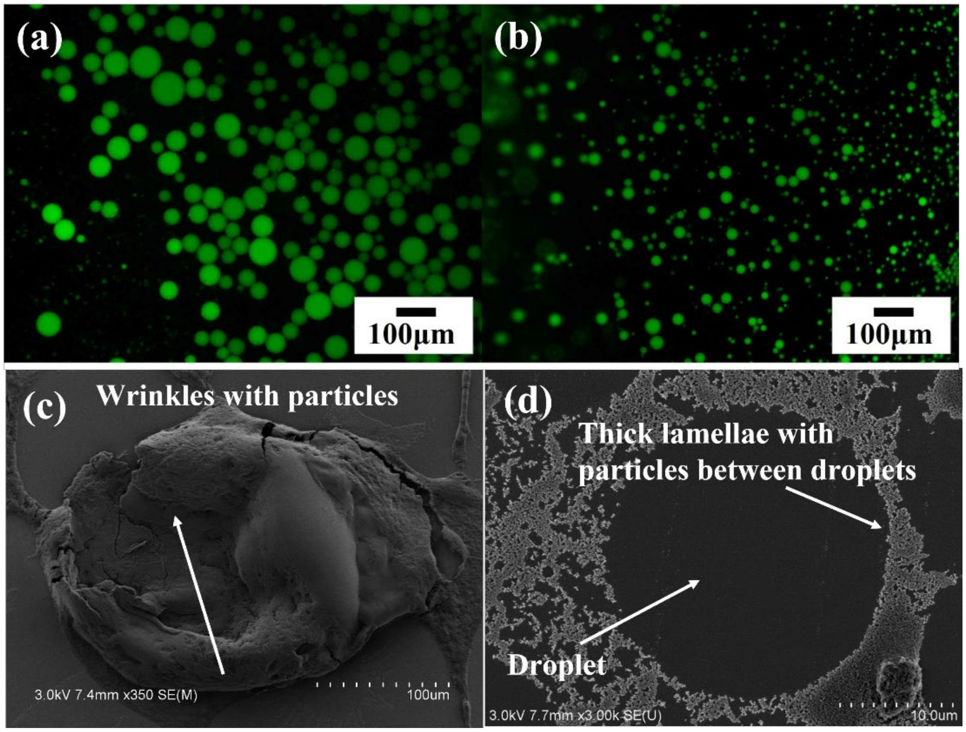


Figure 2. (a, b) Fluorescence micrographs of emulsions (oil stained with Nile red) and (c, d) SEM images of dried emulsions prepared by 0.5 wt.% silica particles and either (a, c) 0.06 mM escin at pH = 4 or (b, d) 0.06 mM SA at pH = 8.

Furthermore, the oil:water ratio of the Pickering emulsions (0.01 mM escin plus 0.5 wt.% silica particles) was freely changed from 2:8 to 7.4:2.6 and high internal phase emulsions (HIPEs) could be obtained at an oil volume fraction of 0.74 (Figure S5). Since the silica particles are too hydrophilic to stabilize an emulsion alone, the synergistic interaction between escin and silica particles enhanced the emulsion stability. Like other nonionic surfactants, escin could adsorb on particle surfaces at pH< 7 through hydrogen bonding between the hydroxyl and silanol groups respectively rendering particles surface-active. Thus, Pickering emulsions were very stable to coalescence due to almost irreversible adsorption of escin-modified silica particles at the droplet interface.

3.2 OID emulsions co-stabilized by SA and silica particles at pH = 8

At alkaline pH of 8, escin was converted to anionic SA which possesses two types of hydrophilic group (carboxylate and hydroxyl). However, no emulsion could be stabilized by escin- alone below 0.06 mM either as shown in Figure S6. After adding 0.5 wt.% silica nanoparticles, stable OID emulsions were prepared above SA concentrations of 0.003 mM (0.048 cmc), Figures 2b and 3. The SEM image revealed spherical oil voids free of particles in the dried emulsions (Figure 2d), indicating that the particles almost remained in the continuous phase. This arrangement is as observed in other OID emulsions of like charged ionic surfactant and particles. [33, 35-38]

The average droplet diameter of the OID emulsion formed by the mixture of 0.003 mM SA and 0.5 wt.% silica was about 100 μm (Figure 3), much smaller than that of the Pickering emulsion (250 μm, 0.5 wt.% silica and 0.003 mM escin, Figure 1c). Similar to our previous studies, the droplet size of OID emulsions was only affected by the SA concentration and not the particle concentration (Figure S7). [33, 35-38]

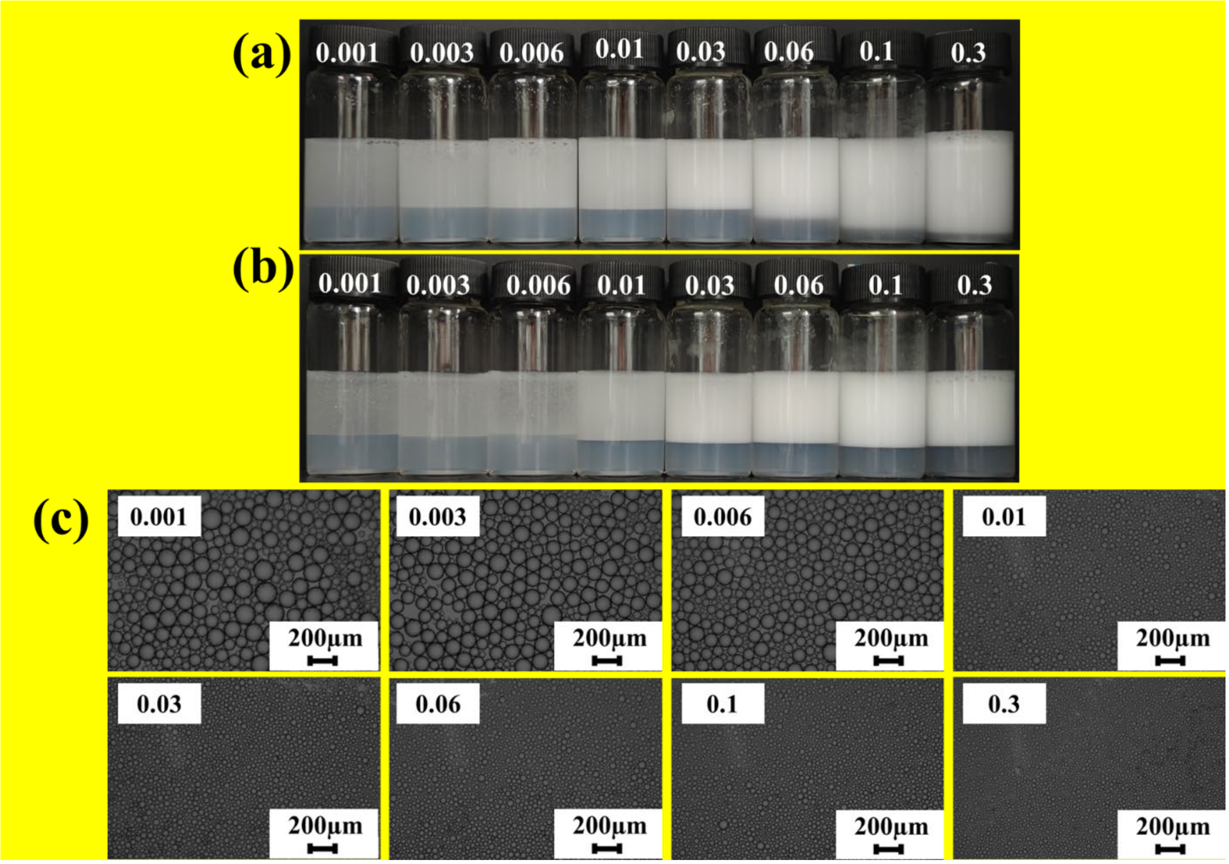


Figure 3. (a, b) Appearance and (c) selected micrographs of OID emulsions prepared by SA (in mM) and 0.5 wt.% silica particles at pH = 8 taken (a) immediately and (b, c) 24 h after homogenization.

The critical concentrations of silica particles and SA surfactant required for the stabilization of OID emulsions were obtained (Figure S8), described by a V-shape curve as plotted in Figure S9. At low surfactant concentration, the minimum particle concentration required for stabilization gradually decreased from 0.30 wt.% to 0.01 wt.% due to synergism between the two species. However, at high SA concentration, the concentration of particles required gradually increased. Here, the ionic surfactant compresses the electrical double layers around the charged particles and droplets acting as an electrolyte, so that more particles were needed to provide enough electrostatic repulsion for emulsion stabilisation.[35-38] Interestingly, high internal phase (up to 74%) OID emulsions could also be obtained with this surfactant-particle mixture (Figure S10).

It is believed that electronic double-layer repulsions are essential for the stability of OID emulsions.[33, 35-38] However, these repulsions could be reduced by adding salt, *e.g.* 0.01 mM NaCl (Figure S11), in which the Debye length was reduced to 96 nm according to DLVO theory.[43] In contrast, the stability of Pickering emulsions (silica particles plus escin at pH = 4) remained high after adding salt (Figure S12) although the average droplet size decreased from 150 μm to 30 μm up to 1 mM NaCl. The adsorption of nonionic escin surfactant on particles may not be affected by addition of low concentrations of salt, whereas added NaCl screens the particle charge facilitating their adsorption to the oil-water interface.[44, 45]

3.3 Electrostatic repulsion *vs* hydrogen bonding in pH-responsive emulsions

Since both escin and SA can stabilize conventional emulsions at high concentrations (> 0.3 mM), the emulsion prepared by 0.6 mM escin was stable after adding NaOH (Figure S13). In contrast, the above Pickering emulsions exhibited pH-responsive behavior due to the interaction between escin and silica particles at low concentrations. Complete demulsification of Pickering emulsions of silica particles and escin occurred after adding NaOH (Figure 4). However, Pickering emulsions stabilised by silica particles coated with a conventional nonionic surfactant $C_{12}E_3$ were stable after alkali treatment (Figure S14). Since escin was converted from nonionic form to anionic form (SA) on raising the pH, the adsorption of SA on particles *via* hydrogen bonding might be inhibited by electrostatic repulsion between similarly charged SA molecules and particles resulting in demulsification. Interestingly, re-homogenization (H) of the above separated mixture of SA and silica particles yielded an OID emulsion with smaller average droplet size (on(2), 30-60 μm, Figure

4c). After addition of concentrated aqueous HCl to the latter emulsion to adjust the pH to 4.0 ± 0.2, the emulsion was rapidly demulsified. Re-homogenization of the demulsified system yielded a Pickering emulsion again (on(3), Figure 4d). The above conversions between Pickering and OID emulsions were fully reversible for at least 4 times by adding NaOH/HCl alternately without significant change of the droplet sizes in the two different types of emulsion.

The change in the micrographs of emulsions containing fluorescent particles evidenced the transformation between a Pickering emulsion and an OID emulsion, in which a bright green interface with a dark inner oil phase and dark continuous phase was observed in the Pickering emulsion (Figures 4e and 4g), while the fluorescent particles preferred to disperse in the continuous phase in the OID emulsion (Figure 4f). [33] The viscosity of the emulsions also exhibited large changes induced by the pH trigger, in which the viscosity of an OID emulsion (8 Pa s) was much lower than that of a Pickering emulsion (88 Pa s) at a shear rate of 0.01 s^{-1}, Figure S15. Similar to reports in the literature, the addition of escin into a dispersion of hydrophilic silica particles endows the particles with surface activity, enabling them to form a solid-like film at the oil-water interface in Pickering emulsions. [5,11] Thus, the viscosity of Pickering emulsions is much higher than that of conventional emulsions stabilized by surfactant or polymer alone. In contrast to Pickering emulsions, SA adsorbs at the oil-water interface in OID emulsions while the silica particles remain dispersed in the aqueous phase. [35-38] Therefore, the viscosity of OID emulsions is close to that of water (at this volume fraction of oil) which is similar to that of conventional emulsions.

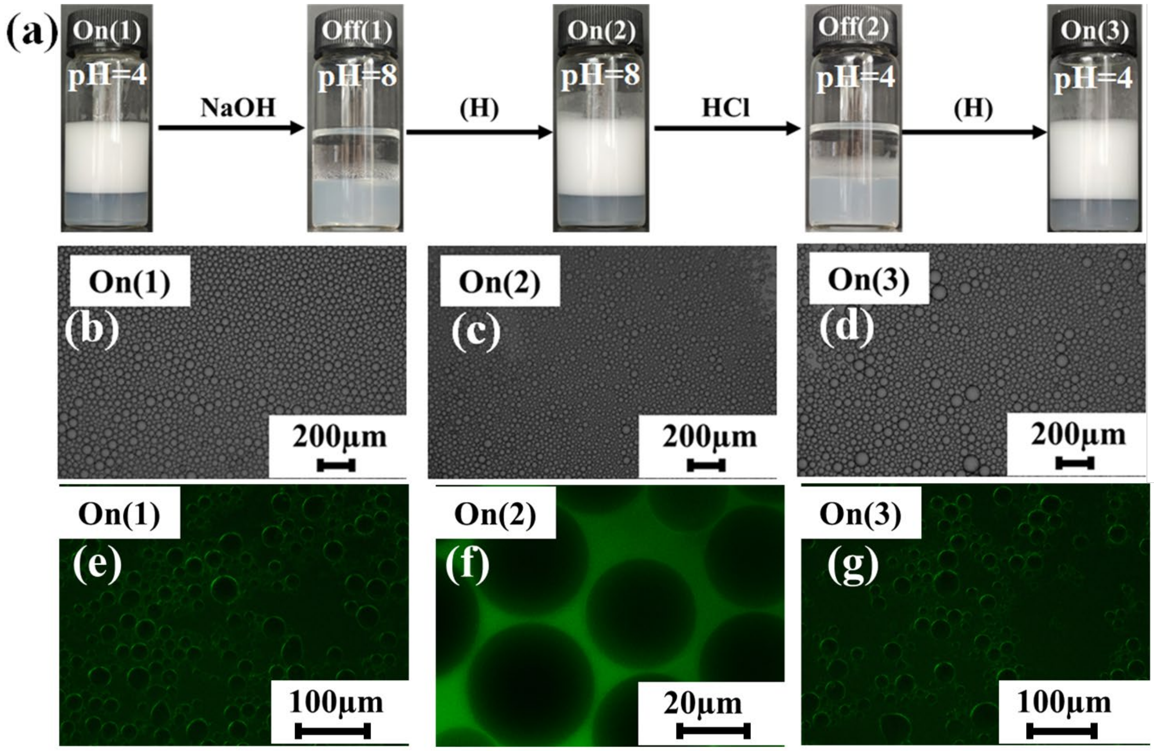


Figure 4. (a) Appearance and (b-d) micrographs of emulsions obtained by 0.06 mM escin/SA and 0.5 wt.% silica particles undergoing switching on/off cycles with pH. Fluorescence microscopy images of (e), (g) Pickering emulsions and (f) OID emulsion using fluorescent particles.

3.4 Mechanism

Adsorption and contact angle measurements were carried out to investigate the interactions between escin and silica particles. The surface tension of escin solutions at pH = 4 increased on addition of silica particles (Figure 5a), indicating that the adsorption of escin molecules on particles reduced the surfactant concentration in solution. For example, at the equilibrium surfactant concentration (0.01 mM), the adsorbed amount of escin was 0.002 mmol/g (148 nm^2/molec.) suggesting monolayer adsorption on particles through hydrogen bonding (Figure 5b). The consequence of escin adsorption was also confirmed by contact angle measurements using the inverted sessile drop method (Figure 5c, Scheme 2).[29] Upon the increase of escin concentration from 0 to 0.03 mM, the contact angle (θ_w) on glass slides (to mimic the surface of silica particles) increased from 21° to 55° (monolayer adsorption), and then decreased to 34° at escin concentrations beyond 0.6 mM because of bilayer/hemi-micelle formation on particles.[12]

The adsorption of escin on particle surfaces was also confirmed by FT-IR of their mixture (Figure S16), where the peaks at 2970-2700 cm^{-1} correspond to ν(C–H) of escin. Hydrogen bonding between escin and silica could be destroyed by adding dimethylformamide, DMF.[46] No stable Pickering emulsion was obtained after addition of DMF (Figure S17), while an OID emulsion co-stabilized by SA and silica particles at pH = 8 was reformed after addition of DMF (Figure S18).

In contrast, the surface tension did not change significantly for SA solutions at pH = 8 upon adding silica particles, which indicated no adsorption of the charged SA on the particles. Furthermore, the θ_w of aqueous solutions of SA remained constant (20-21°, Figure 5d). Although SA molecules contain hydroxyl groups, hydrogen bonding with particle surfaces did not occur. In this case, SA adsorbs at the oil-water interface reducing the interfacial tension and endowing the oil droplets with a negative charge. Similar to other OID emulsions,[33, 35-38] the dominant interaction between SA and silica particles in OID emulsions was changed from hydrogen bonding to electrostatic repulsion.

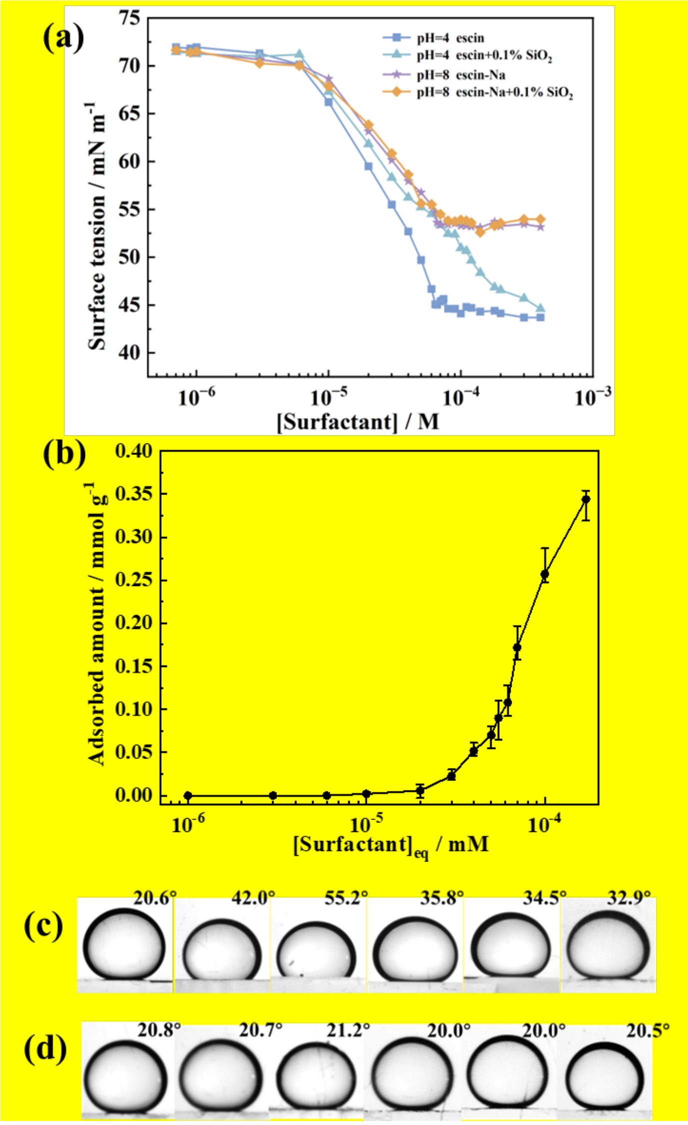


Figure 5. (a) Surface tension of aqueous escin/SA solutions without or with 0.1 wt.% silica particles as a function of initial surfactant concentration at 25 °C, (b) adsorbed amount of escin on particles at pH = 4 as a function of equilibrium escin concentration at 25 °C, (c, d) contact angle of inverted sessile drops of *n*-octane captured by glass slides immersed in aqueous solutions of (c) escin at pH = 4 or (d) SA at pH = 8 at 25 °C. [surfactant] from left to right: 0, 0.01, 0.03, 0.06, 0.1 and 0.3 mM.

Similar phenomena were observed in emulsions co-stabilized by silica particles and polyoxyethylene lauryl ether carboxylate (abbreviated as LCA-3, Figure S19), which has 3 oxyethylene groups adjacent to a carboxylic acid group. Pickering emulsions of high viscosity were stabilized by silica particles containing adsorbed uncharged LCA-3 at pH = 4, while OID emulsions of low viscosity were obtained after LCA-3 was converted into its sodium salt form on adding NaOH (pH=8, Figure 6). The evidence is given in Figure 6d and 6e, where the dried Pickering emulsion droplets at pH = 4 have a clear border with a broken wrinkled particle film. However, voids free of particles were observed in the SEM image of the dried OID emulsion droplets at pH = 8, proving the dispersion of particles in the continuous phase.

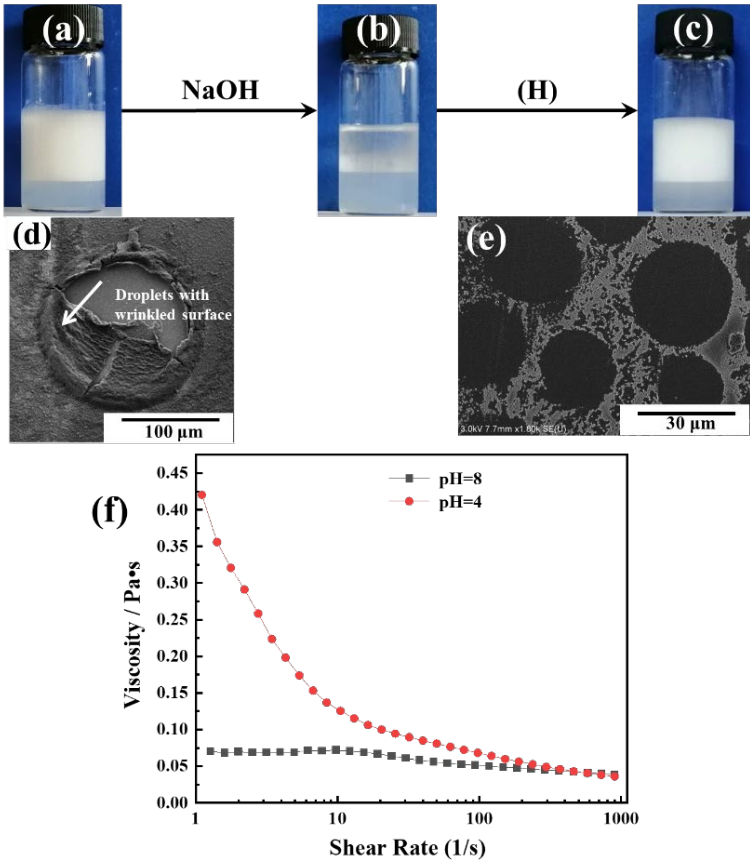


Figure 6. (a-c) the pH responsiveness of the emulsions prepared by a mixture of 0.01 mM LCA-3 and 0.5 wt.% silica particles. (a) Pickering emulsion at pH = 4, (b) demulsification at pH = 8, (c) OID emulsion after re-homogenizing (H) mixture in (b), SEM images of (d) dried Pickering emulsion and (e) dried OID emulsion, (f) viscosity *vs* shear rate of Pickering emulsion in (a) or OID emulsion in (c).

However, such a transformation was not observed in the emulsions prepared by a mixture of a Bola type surfactant (13-polyether (3) tridecanoic acid, abbreviated as PTDA) and silica particles (Figure S20) in which the carboxylic acid group and oxyethylene groups are at either end of the hydrocarbon chain. As shown in Figure S21, although demulsification of a Pickering emulsion could be achieved after adding NaOH, the emulsion co-stabilized by silica particles and sodium 13-polyether (3) tridecanoate (abbreviated as SPTD) was also a Pickering emulsion. Therefore, if the nonionic functional group, *e.g.* hydroxyl or polyoxyethylene, is close to the ionic functional group (such as LCA-3), the hydrogen bonding between surfactant and particles will be destroyed by electrostatic repulsion so that the conversion between a Pickering and an OID emulsion can be achieved (Figure 7). However, if the nonionic functional group is separated from the ionic functional group like in SPTD, the hydrogen bonding between hydroxyl groups of SPTD and silanol groups of silica particles is still achievable at high pH resulting in a Pickering emulsion.

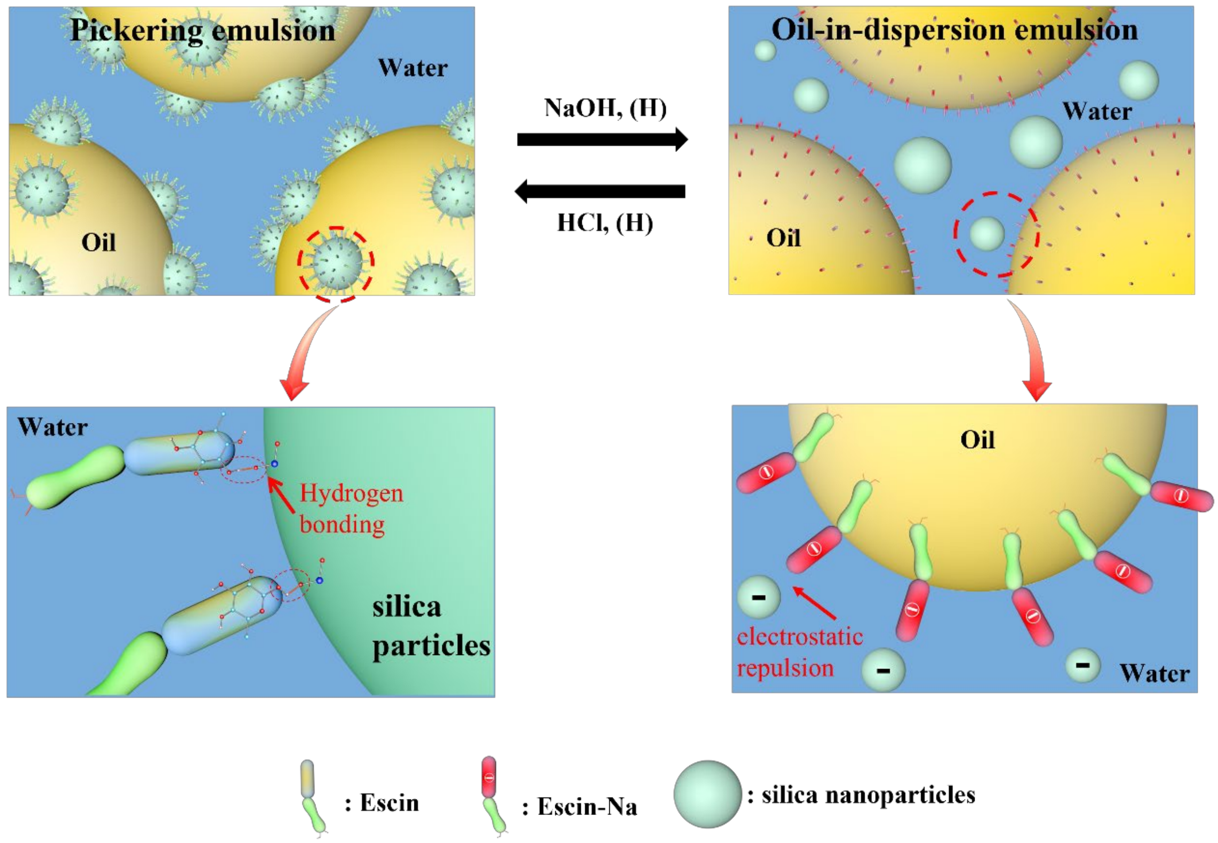


Figure 7. Schematic illustration of inter-conversion of (top left) a Pickering emulsion and (top right) an OID emulsion stabilized by silica particles and escin/SA respectively triggered by pH.

4. Conclusions

We have demonstrated that electrostatic repulsion can inhibit hydrogen bonding between the biosurfactant escin and negatively charged silica nanoparticles and thus induce the transformation from a Pickering emulsion to an OID emulsion triggered by pH. In acidic and neutral media, the nonionic escin adsorbed on silica particle surfaces *via* hydrogen bonds endowing particles with surface activity to stabilize Pickering emulsions. In alkaline media however, escin was transformed into its anionic state (SA) and the electrostatic repulsion overcame the hydrogen bonding resulting in the stabilization of OID emulsions. As a result, the properties of the emulsions such as the emulsion type, viscosity, droplet size and stability could be controlled by pH. This strategy is universal for emulsions stabilized by charged nanoparticles and similarly charged pH-switchable ionic surfactants with nonionic functional groups near to the ionic headgroup (like LCA-3). Such switchable surfactant structure can be further exploited in the development of smart emulsions to fulfill various requirements in different fields, such as controllable stability, tunable droplet size and variable viscosity.

AUTHOR CONTRIBUTIONS

‡ These authors contributed equally to this work.

M.L. performed the investigation, data curation, methodology, software, writing the original draft. J.S. performed the investigation and data curation. B.P.B. performed the writing and reviewing. J.J. performed the conceptualization, methodology, project administration, supervision, funding acquisition, and writing and reviewing. Z.C. performed the writing and reviewing.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21872064).

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