

# Smart Emulsions Stabilized by a Multi-headgroup Surfactant Tolerant to High Concentrations of Acids and Salts

Wanqing Zhang,<sup>a</sup> Bernard P. Binks,<sup>b</sup> Zhenggang Cui,<sup>a</sup> and Jianzhong Jiang<sup>a,\*</sup>

[a] W. Zhang, Prof. Z. Cui, Prof. J. Jiang  
The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical & Material Engineering,  
Jiangnan University, 1800 Lihu Road, Wuxi 214122, China  
E-mail: jzjiang@jiangnan.edu.cn

[b] Prof. B.P. Binks  
Department of Chemistry, University of Hull, Hull. HU6 7RX. UK

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**Abstract:** Retaining emulsions stable at high acidity and salinity is still a great challenge. Here, we report a novel multi-headgroup surfactant ( $C_3H_7-NH^+(C_{10}COOH)_2$ , di-UAPAc) which can be reversibly transformed between cationic, anionic and zwitterionic forms upon pH variation. Stable oil-in-dispersion (OID) emulsions in strong acid (pH = 2) can be co-stabilized by low concentrations of di-UAPAc and silica nanoparticles. High salinity at pH = 2 improves the adsorption of di-UAPAc on silica particles through hydrogen bonding, resulting in the transformation of OID emulsions into Pickering emulsions. Moreover, emulsification/demulsification and interconversion between OID and Pickering emulsions together with control of the viscosity and droplet size can be triggered by pH. The present work provides a new protocol for designing surfactants for various applications in harsh aqueous media, such as strong acidity and high salinity, involved in oil recovery and sewerage treatments.

## Introduction

Emulsions are one of the powerful and promising systems for dispersing one liquid in another immiscible liquid, and have been applied in various fields such as cosmetics,<sup>[1-2]</sup> oil recovery,<sup>[3,4]</sup> and drug delivery.<sup>[5,6]</sup> Emulsion stability is essential in many applications and is affected by various factors, such as the nature of the emulsifier, aqueous salinity and pH.<sup>[7-13]</sup> In some special fields, such as acidic oil recovery and sewerage treatments,<sup>[14-16]</sup> stable emulsions are expected to co-exist with high concentrations of acids and salts. However, in such conditions, conventional emulsions stabilized solely by polymers or surfactants are usually unstable.

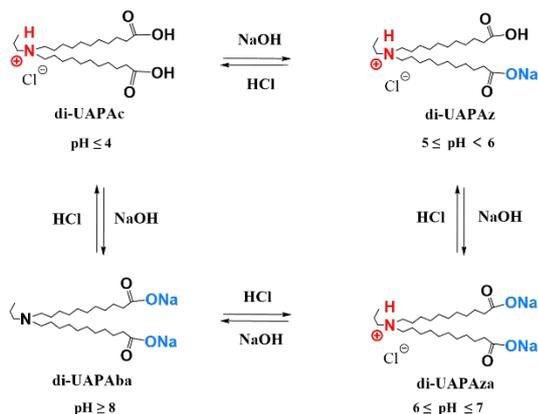
Pickering emulsions are always more stable than conventional emulsions at high salinity due to the protection offered by the colloid particle shell at the oil-water interface.<sup>[6,17-19]</sup> Nevertheless, the morphology, droplet size and surface activity of the particles (like silica) may still be affected by the high concentration of acids or salts,<sup>[20-28]</sup> causing destabilization of Pickering emulsions. Recently, Wang *et al.* reported van der Waals emulsions stabilized solely by hydrophilic silica nanoparticles at pH = 2.5,<sup>[29]</sup> in which the particles surround the oil droplets *via* van der Waals attraction. Such emulsions, however, were not universal and the condition was that the oil phase should possess a high refractive index.

Ionic surfactants were reported to stabilize oil-in-dispersion (OID) emulsions aided by like-charged nanoparticles,<sup>[30-34]</sup> in which the electric double layer repulsions are crucial for emulsion stabilization. However, such repulsion is easily weakened or destroyed in acidic media or with the addition of salts, resulting in demulsification. To date, there is no report on stabilization of OID emulsions at high concentrations of acids or salts. It is still a great challenge to stabilize an emulsion at high concentrations of acids and salts. Herein, we report a novel multi-headgroup surfactant, di-undecanoic acid propylammonium salt ( $C_3H_7-NH^+(C_{10}COOH)_2$ , di-UAPAc), which can co-stabilize OID emulsions in strong acid (pH = 2) with a low concentration of silica nanoparticles (0.1 wt.%). More importantly, the addition of a high concentration of salt ( $\geq 3$  M) up to saturation does not result in demulsification but leads to the conversion of OID emulsions into Pickering emulsions. It is also found that both the OID and Pickering emulsions are pH-responsive. This strategy expands the range of emulsifiers applicable in extreme environments, such as high concentrations of acids and salts, and it is therefore a significant development in emulsion science.

## Results and Discussion

### (a) Structure conversion of di-UAPAc triggered by pH

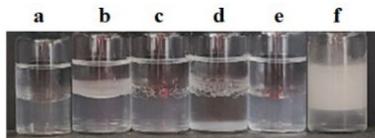
Di-UAPAc contains a tertiary ammonium group and two undecanoic acid chains (Scheme 1). Since di-UAPAc possesses three pK<sub>a</sub> values (8.33, 5.72, 3.71, Figure S1), it can be transformed between a cationic surfactant, (di-UAPAc, pH  $\leq$  4), zwitterionic surfactants  $C_3H_7-NH^+(C_{10}COOH)C_{10}COONa$  (UAPAz, pH = 5-6) and  $C_3H_7-NH^+(C_{10}COONa)_2$  (di-UAPAZa, pH = 6-7) and a bola anionic surfactant ( $C_3H_7-N(C_{10}COONa)_2$ , di-UAPAb, pH  $\geq$  8) at different pH, which were confirmed by <sup>1</sup>HNMR (Figure S2, Tables S1 and S2). For example, at pH = 9, it behaves as a bola anionic surfactant di-UAPAb giving a cmc of 15 mM from oil-water interfacial tension data (Figure S3a). In strong acid (pH = 2), di-UAPAc behaves as a single head, double tail cationic surfactant which shows no cmc up to 3 mM (Figure S3a) and solutions with higher concentrations become turbid. However, the interfacial tension curve (Figure S3a) gives a cross-sectional area of 1.19 nm<sup>2</sup>/molec., which is double that of CTAB (0.53 nm<sup>2</sup>/molec.) a typical cationic surfactant (Figure S3b, Table S3).



**Scheme 1.** Chemical structure of di-undecanoic acid propylammonium salt (di-UAPAc) and its multi-forms triggered by pH.

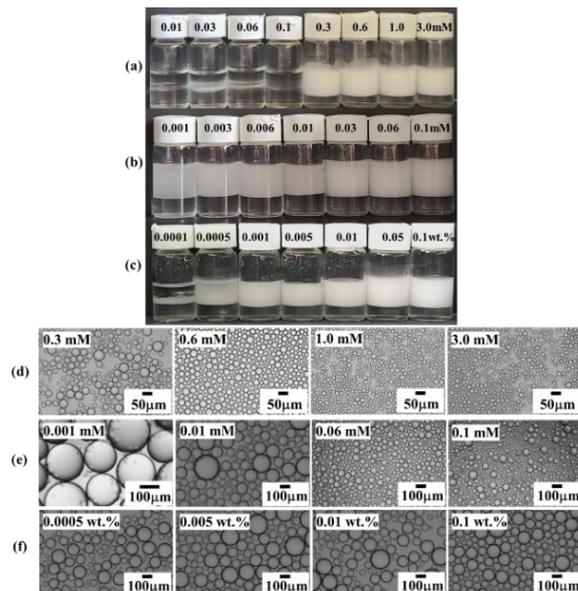
### (b) Stable O/W emulsions in strong acid (pH = 2)

In strong acid (pH = 2), commercial hydrophilic silica nanoparticles (primary diameter 20 nm, average aggregate size = 180 nm, zeta potential ( $\zeta$ ) = +4 mV, (Figure S4) cannot stabilize O/W emulsions alone (*n*-octane: water volume ratio = 1:1 for all emulsions), as shown in Figure 1a and Figure S5). On addition of a low concentration (0.01 mM) of a conventional surfactant such as cationic CTAB, anionic SDS or nonionic Tween-80 and AEO-9 into the silica dispersions (0.1 wt.%), no stable emulsion was obtained either (Figure 1). Interestingly, a stable O/W emulsion was formed after adding 0.01mM di-UAPAc into the silica dispersion (Figure 1).



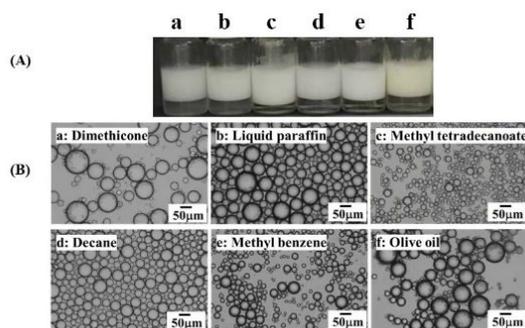
**Figure 1.** Photos of *n*-octane-in-water emulsions at pH = 2 (O:W volume ratio = 1:1) prepared with: (a) 0.1 wt.% silica particles alone; (b-f) 0.1 wt.% silica particles plus 0.01 mM surfactant, taken 24 h after homogenization. Surfactant: (b) CTAB, (c) AEO-9, (d) Tween 80, (e) SDS, (f) di-UAPAc.

Although di-UAPAc cannot stabilize an emulsion alone at a concentration below 0.3 mM (Figure 2a), a systematic study shows that mixtures of di-UAPAc and slightly positively charged silica particles can co-stabilize O/W emulsions at very low concentrations (0.001 mM and 0.001 wt.%, respectively) at pH = 2. The emulsion droplet size decreases from 180  $\mu$ m to 30  $\mu$ m upon increasing the concentration of di-UAPAc from 0.001 mM to 0.1 mM (Figure 2e), whereas it remains almost constant (60-70  $\mu$ m) for various concentrations of silica particles (Figure 2f and Figure S6d,e). These characteristics suggest that the emulsions formed are O/W emulsions,<sup>[30-35]</sup> which were confirmed by the optical and fluorescence micrographs using labeled silica particles (Figure S7), in which particles were observed to disperse in the aqueous phase and not adsorb at the oil-water interface. Furthermore, this mixed emulsifier is effective for emulsifying other oils such as liquid paraffin, aromatic hydrocarbon, triglycerides and silicone oil, and in the presence of other acids such as sulphuric acid and nitric acid to control pH (Figure S8).



**Figure 2.** (a-c) Photos and (d-g) optical micrographs of O/W emulsions prepared at pH = 2 stabilized by different emulsifiers, taken 24 h after preparation. (a, d) di-UAPAc alone at different concentrations; (b, e) 0.1 wt.% silica particles plus di-UAPAc at different concentrations; (c, f) 0.01 mM di-UAPAc plus different concentrations of silica particles.

We have measured the *n*-octane-water contact angle ( $\theta_w$ ) on both glass slides (to mimic the surface of silica particles) (Figure S9) and pressed silica nanoparticle sheets (Figure S10) immersed in a surfactant solution of pH = 2 by the captured oil drop method, and obtained similar  $\theta_w$  values. As shown in Figure S9, the captured oil drops are almost spherical giving  $\theta_w$  of  $11^\circ \pm 2^\circ$  at di-UAPAc concentrations below 0.3 mM. This indicates that the inherent wettability (strongly hydrophilic) of the silica particles is not changed in the presence of di-UAPAc.



**Figure 3.** (A) Photos and (B) optical micrographs of O/W emulsions stabilized by 0.01 mM di-UAPAc and 0.1 wt.% silica particles with different oils at pH = 2 taken 24 h after homogenization.

This prediction is further confirmed by interfacial tension measurements (Figure S3), where the interfacial tension after adding 0.1 wt.% silica particles is slightly lower than that without particles. If di-UAPAc was adsorbed by particles, the interfacial tension would have increased. Therefore, the presence of silica nanoparticles improves the adsorption of di-UAPAc to the oil-water interface at pH = 2 through electrical repulsions. However, such an increase in the adsorption of the surfactant at the interface is quite limited at low particle concentrations. Furthermore, the addition of silica particles will increase the

distance between the droplets (Figure S11) and the van der Waals attraction between the droplets can be significantly reduced, which prevents them from flocculation or coalescence.

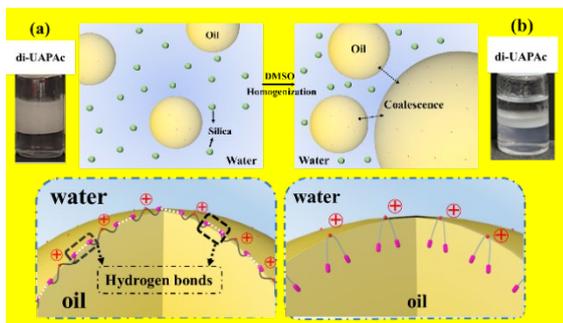
In previous studies, we reported that a critical zeta potential  $\zeta$  of the particles,  $\pm 18$  mV,<sup>[31]</sup> is essential for the formation of OID emulsions. However, in this system, the strongly acidic medium brings excessive ionic strength which leads to a significant decline of the zeta potential to  $+(1-4)$  mV in the absence or presence of di-UAPAc (Figure S4c,d). The particle-particle and particle-droplet repulsions are not as high as those in typical OID emulsions.<sup>[30-32]</sup> This may explain why OID emulsions cannot be co-stabilized by silica particles and other cationic surfactants like CTAB, di-dodecyltrimethylammonium bromide(di-C<sub>12</sub>DAB) and undecanoic acid dimethylamine (N(CH<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>COOH), shown in Figure 1b and Figure S12.

It is believed that there is also a critical  $\zeta$  of oil droplets for stabilizing OID emulsions. Although it is difficult to measure, the  $\zeta$  of oil droplets can be analyzed by the interfacial potential of the oil droplets ( $\phi^o$ ), which can be calculated based on equation (1)<sup>[35,36]</sup>:

$$\phi^o = 51.4 \sinh^{-1} \left[ \frac{8.24 \times 10^9 \Gamma_{R+}}{\sqrt{C_s}} \right] \text{ (mV)} \quad (1)$$

where  $\Gamma_{R+}$  is the adsorbed amount of surfactant at a certain concentration and  $C_s$  is the counterion concentration (the total concentration of cationic surfactant and HCl here). The result gives that  $\phi^o$  decreases significantly from 312 mV at pH = 7 to 174 mV at pH = 2 for *n*-octane-in-CTAB solution droplets (0.01 mM). However, droplets of *n*-octane-in-di-UAPAc solution (0.01 mM) give a much lower  $\phi^o$  (164 mV) at pH = 2 but the OID emulsions formed are stable, suggesting other mechanisms are present in this system.

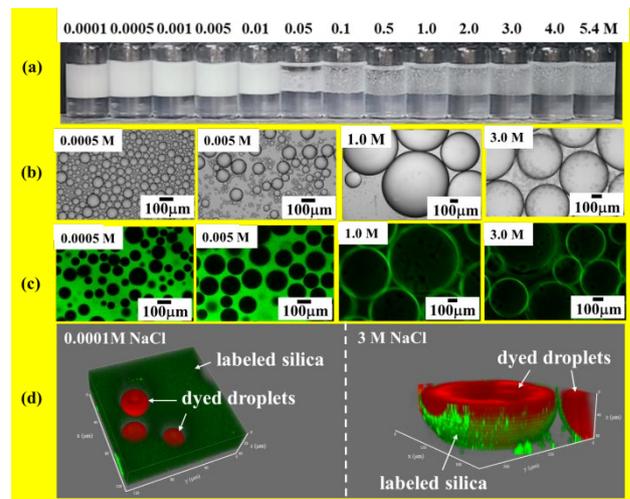
It is suggested that hydrogen bonds between carboxylic acid groups in di-UAPAc may assist in emulsion stabilization despite the decreased electrostatic repulsion. Form molecular dynamics simulation, the carboxylic groups of di-UAPAc are arranged at the oil-water interface with a bent shape of C<sub>10</sub> chains (Figure S13),<sup>[37,38]</sup> In this way the adsorbed di-UAPAc molecules may form a dense and tough film against coalescence at low concentration ( $\Gamma_{R+} = 1.28 \times 10^{-10}$  mol/cm<sup>2</sup> at 0.01 mM), as shown in Figure 4 which makes it possible for di-UAPAc to stabilize O/W emulsions at pH = 2 either alone or together with silica particles at concentrations much lower than those required for other surfactants. This suggestion is further confirmed by the demulsification of the emulsions upon the addition of dimethyl sulfoxide (DMSO), a hydrogen bond breaker,<sup>[39-41]</sup> as shown in Figure 4b.



**Figure 4.** Photos and schematic of the microstructure of OID emulsions (0.01 mM di-UAPAc and 0.1 wt.% silica particles) at pH = 2. (a) Before and (b) after adding DMSO (150  $\mu$ L in 8 mL emulsion) taken after 24 h.

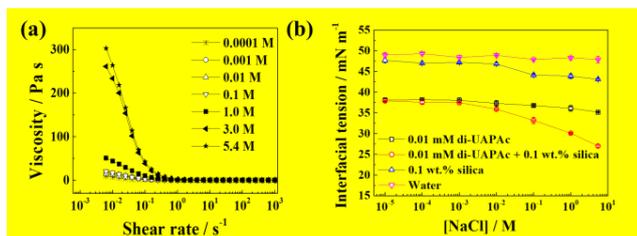
### (c) Stable emulsions at high salinity (pH = 2)

It is known that OID emulsions are sensitive to salts<sup>[30]</sup> because they weaken or destroy the electric double layer repulsion leading to demulsification. After adding low concentrations of NaCl ( $\leq 0.005$  M), the stability of the OID emulsions was decreased from 5 days to 3 days (Figures S14 and S15), and no stable emulsions can be observed after 3 days at  $C_{NaCl}$  between 0.05 and 0.5 M due to the weakened repulsion. Interestingly, the stability of the emulsions was improved from 7 days ( $C_{NaCl} = 1-2$  M) to over 30 days ( $C_{NaCl} \geq 3$  M) at high salinity (Figure S16). At low NaCl concentration the emulsions are OID type whereas at high  $C_{NaCl}$  ( $\geq 1$  M) they convert to Pickering emulsions, as evidenced by the optical and fluorescence micrographs with labeled particles (Figures 5b, 5c and S17). Such transformation from an OID emulsion to a Pickering emulsion can also be achieved in the presence of higher valency salts such as Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> and FeCl<sub>3</sub> (Figure S18). Similar to other OID emulsions, the average droplet size increased upon increasing low concentrations of NaCl ( $\leq 0.01$  M) (Figures 5c, 5d and S19). But once the emulsion becomes a Pickering emulsion ( $C_{NaCl} \geq 1$  M), the droplet size decreases with increasing  $C_{NaCl}$  (Figures 5b, S19, and S20). For example, the droplet size decreased from 700  $\mu$ m at  $C_{NaCl} = 1$  M to 480  $\mu$ m at  $C_{NaCl} = 3$  M (Figure 5b). Accordingly, the emulsion viscosity changes from fluid-like ( $C_{NaCl} \leq 0.01$  M) to highly viscous at high  $C_{NaCl}$  ( $\geq 3$  M) and reaches a viscosity of 300 Pa s (shear rate = 0.01 s<sup>-1</sup>) at  $C_{NaCl} = 5.43$  M (Figure 6a). The conversion of an OID emulsion into a Pickering emulsion was confirmed by the 3D z-stack CLSM images. As illustrated in Figure 5d, the oil drops (stained by Nile red) were coated with green particles in the Pickering emulsion at  $C_{NaCl} = 3$  M, while the surface of oil droplets at  $C_{NaCl} = 0.0001$  M was devoid of green particles in the OID emulsion. Such conversion was further confirmed by UV curing of the emulsion droplets (Figure S21), in which the solid polymer spheres formed at low  $C_{NaCl}$  (0-0.005M) have a smooth surface, but those at high  $C_{NaCl}$  (1-3 M) possess a rough surface as silica particles are adsorbed at the original oil-water interface. Therefore, the salt-induced conversion from OID emulsions to Pickering emulsions endows them with excellent stability against strong acid and high salinity ( $\geq 3$  M).



**Figure 5.** (a) Photos of O/W emulsions (0.01 mM di-UAPAc + 0.1 wt.% silica particles) at pH = 2 at different NaCl concentrations (shown in M) taken 24 h after preparation; (b, c) selected optical and fluorescence micrographs using labeled silica particles; (d) 3D z-stack

CLSM images of emulsions at (left)  $C_{\text{NaCl}} = 0.0001 \text{ M}$  and (right)  $C_{\text{NaCl}} = 3 \text{ M}$  using labeled silica particles and dyed droplets



**Figure 6.** (a) Viscosity versus shear rate for O/W emulsions (0.01 mM di-UAPAc plus 0.1 wt.% silica particles) at different  $C_{\text{NaCl}}$  (in M) at pH = 2; (b) interfacial tension between *n*-octane and aqueous solutions with or without 0.01 mM di-UAPAc/0.1 wt.% silica particles as a function  $C_{\text{NaCl}}$  at pH = 2 (25 °C).

It has been reported that hydrophilic silica particles could be surface modified to stabilize Pickering emulsions by adding indifferent salts or surface-active electrolytes where the particles flocculated at the oil-water interface above a critical concentration.<sup>[42-44]</sup> In this system, however, the  $\zeta$  of the particles only decreases from + 1.8 mV to 0 mV upon increasing  $C_{\text{NaCl}}$  to 0.1 M (Figure S22a) because the charges on silica particle surfaces have been significantly screened by the high concentration of acid. Similarly, with increasing  $C_{\text{NaCl}}$  from 0.0001 M to saturation (5.43 M),  $\theta_w$  at pH = 2 shows a slight increase from 10° to 26° (Figure S23) and the oil-silica dispersion interfacial tension decreases gradually from 47.7 mN m<sup>-1</sup> to 43.1 mN m<sup>-1</sup> (Figure 6b). The interfacial tension does not change however for silica particles at neutral pH. Although flocculation of silica particles was observed in dispersions at  $C_{\text{NaCl}} \geq 0.1 \text{ M}$  at pH = 2 (Figure S24), no stable emulsions could be formed using silica particles alone after adding NaCl (0.05-5.43 M, pH = 2, Figure S25). These results suggest that the wettability alteration of particles in strong acid by the addition of NaCl alone is not enough to enable the stabilization of Pickering emulsions. The presence of the surfactant is therefore crucial in this situation.

The interfacial tension of di-UAPAc solution (0.01 mM) and dispersions (0.1 wt.% silica particles plus 0.01mM di-UAPAc) as a function of  $C_{\text{NaCl}}$  was measured, as shown in Figure 6b. At low  $C_{\text{NaCl}}$  (< 0.001 M), the interfacial tensions of the dispersions are almost the same as that of the solutions indicating no adsorption of di-UAPAc on particle surfaces, in accordance with the low  $\theta_w$  (~13°) of 0.01 mM di-UAPAc solution on a glass surface (Figure S23). At high  $C_{\text{NaCl}}$  ( $\geq 0.1 \text{ M}$ ), the interfacial tension of the dispersions is distinctly higher than that of the solutions (33-37 mN/m), suggesting adsorption of di-UAPAc on particles which have a  $\zeta$  approaching zero (Figure S22). The particles are then turned to slightly surface-active and can stabilize Pickering emulsions with larger droplets (~700  $\mu\text{m}$ ,  $C_{\text{NaCl}} = 1 \text{ M}$ ).

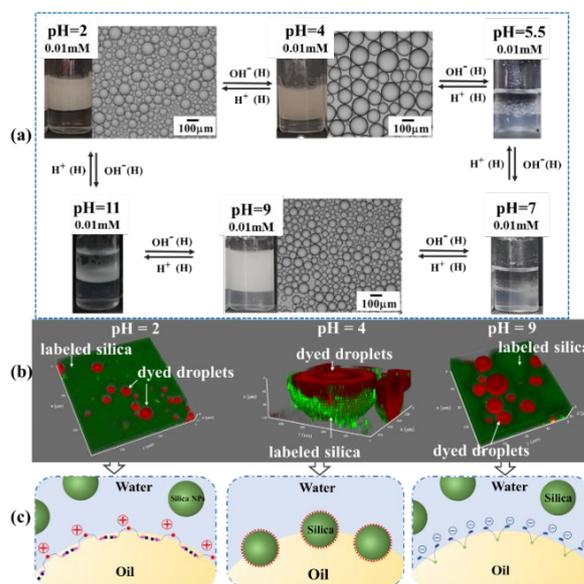
The difference in interfacial tension between dispersions and solutions becomes larger with increasing  $C_{\text{NaCl}}$  (> 0.1 M, Figure 6b), suggesting an increase in surfactant adsorption on particles which can also be confirmed by the increase in  $\theta_w$  (0.01 mM di-UAPAc solution) on glass slides at pH = 2 from 13° at  $C_{\text{NaCl}} = 0.1 \text{ M}$  to 43° at  $C_{\text{NaCl}} = 5.43 \text{ M}$  (Figure S23). It is suggested that di-UAPAc molecules adsorb on particle surfaces through hydrogen bonds between the carboxylic acid groups and silanol groups, which hydrophobizes the particles *in situ*. It was also reported that the addition of NaCl led to more hydrogen bonding among soy hull polysaccharide (SHPA) molecules in the formation of

emulsions.<sup>[45]</sup> Increasing  $C_{\text{NaCl}}$  improves the adsorption of di-UAPAc on particles and thus enhances their surface activity leading to smaller oil droplet sizes in the Pickering emulsions formed (Figures 5 and S23). Furthermore, the estimated coverage of particles on the surface of oil droplets based on the droplet sizes and adsorbed particle amounts increased from 32.9% to 43.6% on increasing  $C_{\text{NaCl}}$  from 1 M to 4.5 M (Table S4), which confirms the improvement of particle adsorption at the oil-water interface on increasing salinity. On the other hand, the hydrogen bonding is sensitive to various external factors, and here demulsification was observed on heating the Pickering emulsion to 45 °C for 30 min or on the addition of 200  $\mu\text{L}$  DMSO into the emulsion (Figure S26).

The viscoelasticity of Pickering emulsions shows an elastic behavior in which the loss modulus ( $G''$ ) was lower than the storage modulus ( $G'$ ) throughout the whole frequency range (Figure S27). Both  $G'$  and  $G''$  of the Pickering emulsions at high NaCl concentrations (3-5.4 M) are much higher than those of OID emulsions at 0.0001 M NaCl, due mainly to the adsorption of silica particles at the oil-water interface in the former.

#### (d) pH-responsiveness of emulsions

Since both the tertiary amine and carboxylic acid groups in di-UAPAc are pH-responsive, the effect of pH on the formation and stability of the emulsions was examined. It is found that O/W emulsions can be formed by the mixed emulsifier (0.01 mM di-UAPAc plus 0.1 wt.% silica particles) at different batch pH except at pH = 5-8 and pH > 11, as shown in Figure S28. The findings were similar if the pH of an emulsion was varied continuously upon adding NaOH or HCl (Figure 7). To understand the mechanism, the viscosity of the emulsions and the wettability of particles at different pH were evaluated (Figure 8).

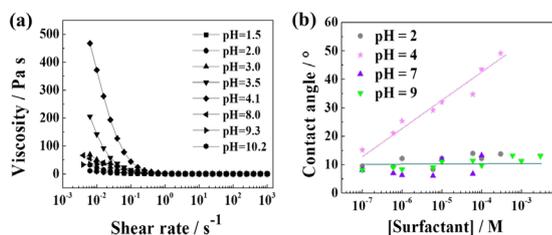


**Figure 7.** (a) Photos and optical micrographs of O/W emulsions at different pH co-stabilized by 0.1 wt.% silica particles and 0.01 mM surfactant taken 24 h after preparation; (b) 3D z-stack CLSM images of emulsions at different pH using labeled silica particles and dyed droplets; (c) schematic of the emulsions. Surfactant is: di-UAPAc, pH  $\leq 4$ ; di-UAPAc, 5  $\leq$  pH < 6; di-UAPAc, 6 < pH  $\leq$  7; di-UAPAc, pH > 8.

As discussed above, the OID emulsions at pH = 2 are of a relatively small droplet size (50-100  $\mu\text{m}$ ). By adding NaOH to

increase the pH to 4, O/W Pickering emulsions are formed of larger droplet size (100-200  $\mu\text{m}$ ), higher viscosity and high stability (> 30 days, Figure S29) with the microstructure being proved by fluorescence microscopy using labeled silica particles (Figure 7, Figure S30b, Figure S31d). Meanwhile, the  $\zeta$  of silica particles in pure water was reversed from +4 mV (pH = 2) to -8.8 mV (pH = 4). Cationic di-UAPAc molecules will adsorb on negatively charged particle surfaces at pH = 4 (Figure S30), ending the particles with surface activity to stabilize Pickering emulsions. Therefore, packing of small silica particles was observed on the 3D z-stack CLSM images (Figure 7b) and on the surface of the polymer spheres formed by UV- polymerization of Pickering emulsion droplets at pH = 4, while a surface free of silica particles was observed for those formed from OID emulsions at pH = 2 or 9 (Figures 7b and S32). The adsorption of surfactant on particles at pH = 4 is supported by interfacial tension measurements since that of a di-UAPAc solution (0.01 mM) containing dispersed silica particles (0.1 wt.%) is higher than that of a solution without particles (Figure S33). Furthermore, the  $\zeta$  of silica particles changes from -3.4 mV to -1.1 mV after increasing di-UAPAc concentration from 0.001 mM to 0.1 mM (Figure S34a), suggesting charge neutralization.  $\theta_w$  on glass slides increases from 25° to 43° upon increasing the di-UAPAc concentration (Figure 8b, Figure S35a), indicating monolayer adsorption of surfactant on particles. Therefore, at pH = 4, the *in situ* hydrophobized silica particles stabilize a Pickering emulsion.

The reversible conversion between OID and Pickering emulsions (di-UAPAc plus silica particles) is triggered by pH between 2 and 4. Specifically, the transformation can be cycled at least 10 times (Figure S36) by the pH trigger despite the accumulation of NaCl. However, with the accumulation of NaCl beyond 0.1 M, the transformation is no longer possible as the OID emulsion at pH = 2 is itself converted to a Pickering emulsion.



**Figure 8.** (a) Viscosity as a function of shear rate for batch octane-in-water emulsions at different pH. [surfactant] = 0.01 mM, [silica] = 0.1 wt.%. (b) Contact angle through water as a function of [surfactant] at different pH.

At  $5 \leq \text{pH} < 6$ , the surfactant is converted to one of the zwitterionic forms di-UAPAz (Scheme 1) and cannot stabilize an emulsion alone or in the presence of silica particles below 0.3 mM (Figure S37). This is due to the neutralization of the positive charge ( $\text{NH}^+$ ) by the negative charge ( $\text{COO}^-$ ) in the surfactant molecule. Similarly at  $6 < \text{pH} \leq 7$ , the surfactant is changed to the other zwitterionic form di-UAPAz (Scheme 1) where both COOH groups are charged and cannot stabilize emulsions with or without silica particles (Figure S38). In both cases (pH = 5.5 and 7.0), the zwitterionic surfactants do not adsorb on particles to improve their wettability as shown by the small changes in the  $\zeta$  value (Figure S34b) and contact angles (Figures S35b and S35c) with increasing surfactant concentration.

At pH > 8, the surfactant is converted to a bola anionic one (di-UAPAb) which can co-stabilize OID emulsions together with

negatively charged silica particles with a stability of 6 days (Figures S39 and S40).<sup>[30-32]</sup> Unlike the OID emulsions at pH = 2, the OID emulsions formed at pH = 9 are sensitive to salt accumulation (Figure S41), and the cycling is limited (only twice between pH = 2 and pH = 9, (Figure S36a)). This is because di-UAPAb behaves as a conventional anionic surfactant where electrostatic repulsion is important for emulsion stabilization but is easily destroyed by the addition of salt. Therefore, OID emulsions cannot be formed at low concentrations of di-UAPAb at pH = 11 due to the high ionic strength in the solution.

The requirements for emulsion properties differ in different applications, e.g. temporary stability and demulsification are needed in organic synthesis<sup>[42]</sup> and emulsion polymerization,<sup>[35,46,47]</sup> high stability and high viscosity are preferred in emulsion adhesive and coating formulations<sup>[1,2,48]</sup> but low viscosity and high stability are favored for cutting emulsions and in pipeline transportation of oils.<sup>[49,50]</sup> The novel functional surfactant developed here is of great importance for delivering particular special requirements of emulsions in potential applications.

## Conclusions

In summary, a novel multi-headgroup surfactant was synthesized which can be reversibly transformed between single-head, double tail cationic di-UAPAc, zwitterionic di-UAPAz and di-UAPAz as well as bola anionic di-UAPAb forms triggered by pH. Stable OID emulsions can be prepared using di-UAPAc and hydrophilic silica particles both at very low concentrations at pH = 2, where the particles are slightly positively charged. Hydrogen bonding between carboxylic acid groups in di-UAPAc allows the formation of a tough surfactant film at the oil-water interface, beneficial for stabilizing OID emulsions in strong acids. Increasing the NaCl concentration (up to saturation) or that of other salts at pH = 2 promotes the adsorption of cationic di-UAPAc on particle surfaces via hydrogen bonding between the -COOH group and Si-OH groups on particles such that particles are hydrophobized *in situ* and become capable of stabilizing Pickering emulsions, resulting in changes in viscosity and droplet size. Furthermore, emulsions of surfactant and silica particles have particular pH responsiveness due to the reversible transformation between cationic, zwitterionic and anionic surfactant forms in which “on-demand” stability and reversible transformation between OID and Pickering emulsions together with droplet size and viscosity can be triggered by pH. This research provides a new tactic for the design of surfactant structures for the stabilization of emulsions in harsh conditions such as in both high acidity and high salinity, which may be involved in potential applications such as oil recovery and sewerage treatment, and for emulsions with multiple requirements of stability, droplet size and viscosity.

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## Conflict of interest

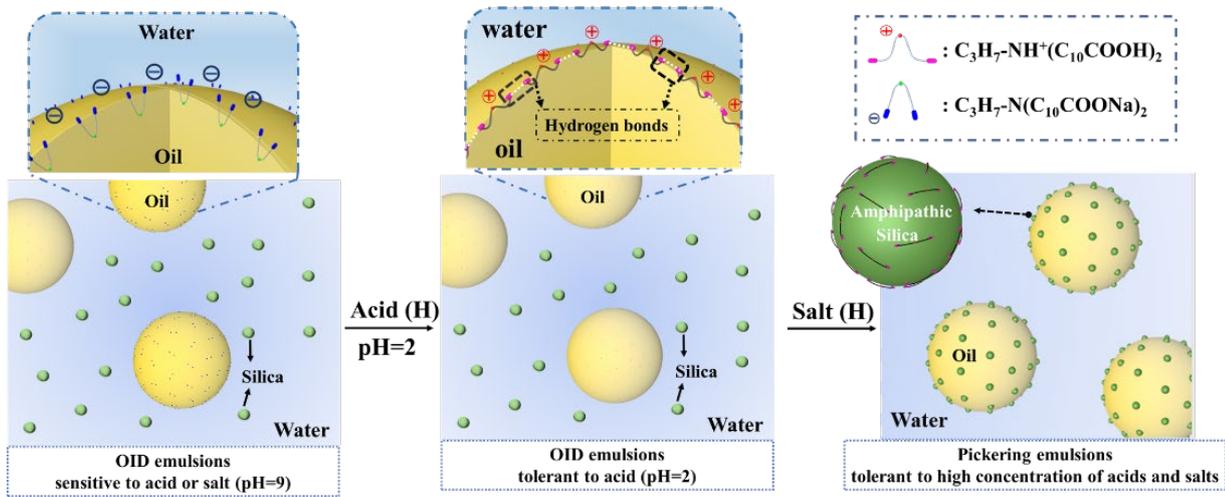
The authors declare no conflict of interest.

**Keywords:** emulsions; strong acid; salt; stability; pH-responsiveness.

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## Entry for Table of Contents



A multi-headgroup surfactant was synthesized that can be transformed between cationic (di-UAPAc), zwitterionic and bola structures by pH trigger. In strong acid, di-UAPAc co-stabilizes OID emulsions in combination with silica particles which convert to Pickering emulsions upon addition of high concentration of salts.

replace label Amphipathic by Surface-active