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Journal Name

ARTICLE

Highly stable aqueous foams generated by fumed silica particles hydrophobised *in situ* with a quaternary ammonium gemini surfactant

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Commercially available fumed silica (F-SiO₂) was hydrophobised *in situ* via the interaction with a cationic gemini surfactant, ethanediyl- α,ω -bis(tetradecyldimethyl-ammonium bromide) (14-2-14), in aqueous solution. The effect of this surfactant modification was far higher than that carried out by its corresponding monomer, tetradecyltrimethylammonium bromide (C₁₄TABr). The mechanism of modification was assumed according to zeta potential measurements and observations of physical appearance. These particles were used to generate and stabilize aqueous foams. Both the foaming efficiency and the stabilising ability of F-SiO₂/14-2-14 all exceeded that of F-SiO₂/C₁₄TAB. In the gemini case, the synergism and competition between the particles and the free surfactant molecules for their adsorption at the foam film were found, which resulted in two peaks in the foam stability curve. Dilational rheology of the films was measured using an oscillating drop technique. There were also two maxima in the dilational elasticity ε for the F-SiO₂/14-2-14 system, respectively corresponding to each maximum in foam stability.

1. Introduction

Aqueous foams are important in a variety of different applications, ranging from food and cosmetics to oil recovery, blast mitigation, and fire extinguishing.^{1,2} Recently, foams have been extensively used in the development of new materials,³⁻⁵ or as vehicles for drug delivery.⁶⁻⁸ Compared with emulsions, the long-term stability of aerated foams is much more difficult to achieve.² Due to their technological and commercial significance, research into foams has attracted increasing attention.

Similar to surfactants, solid colloidal particles with suitable wettability can spontaneously accumulate at the liquid surface to form particle monolayers,⁹ by which foams are well stabilised. Different type of particles, of nanometre to micron size, have been used, for example, silica,^{10,11} latex,^{12,13} metal,^{14,15} etc. Most of these particles were spherical, and only a few were non-spherical and these included disks¹⁶ and ellipsoids.¹⁷ The state of aggregation of particles in a monolayer depends on their shape, for example, non-spherical particles form loose aggregates with a network-like structure.^{16,17} Due to a significant deformation of the fluid interface around non-spherical particles, these irregular shape particles generate

significant capillary attraction, which increases the shear elasticity when in monolayer form.¹⁷⁻¹⁹ Research interest was expanded to include fumed silica particles.^{9,20} Fumed silica is made by burning volatile silanes, such as silicon tetrachloride. Although primary particles are only a few nanometres in diameter, the products, after cooling, show a form of agglomeration of particle aggregates and thereby have very irregular shapes.²¹ The fumed silica particles adsorbed at the liquid interface has been found to yield long-term stability for emulsions.²² Therefore, high-stability foams can be expected when using fumed silica as a stabiliser.

Solid particles need to be surface-treated, which will yield a suitable wettability for their subsequent adsorption. The wettability of particles at the air/water interface has been known to be crucial in optimising the stability of solid-stabilised foams.⁹ A popular route is to coat nanoparticles homogeneously, however, this can greatly increase the cost of the particles. The other cheap and convenient route is to modify the particles *in situ* in aqueous media via interaction with amphiphilic compounds.^{23,24} Comparatively, this surface activation of nanoparticles is less complicated and inexpensive and is therefore of practical significance.

In the present work, we were interested in commercially available fumed silica particles as a foam stabiliser: these have highly irregular shapes and did not go through a special hydrophobic-treatment as general in refs.²⁵⁻²⁷ The modification of the fumed silica particles was carried out *in situ* in an aqueous solution of a gemini-type cationic surfactant, ethanediyl- α,ω -bis(tetradecyldimethylammonium bromide) (14-2-14). Thus, this work can be expected to show (1) the shape effect of irregular particles on stabilizing foams; (2) a

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direct use of commercial fumed silica without any hydrophobic-treatments, which favoured future popularization in practical applications; and (3) the highly-effective role of gemini surfactant. Gemini surfactants have the ability to adsorb on two-phase interfaces to a much greater extent than traditional single-tail amphiphiles.²⁸ In particular, the chosen 14-2-14 surfactant here had a short spacer and this structure made it more adsorbent than a gemini carrying a long spacer. Moreover, 14-2-14 itself has been demonstrated to be a good stabiliser in aqueous foams.^{29,30} It was certainly interesting when the two components, fumed silica and 14-2-14, were met because the both were highly active for their interfacial behaviour. For comparison, the corresponding monomer of 14-2-14, tetradecyltrimethylammonium bromide (C₁₄TABr), was also examined in this work.

2. Experimental work

2.1. Materials

The commercial fumed silica (F-SiO₂) involved in this work was Aerosil 200 (purity ≥ 99.8%, produced by Degussa Co., Germany) and its TEM image is shown in Fig. 1. The F-SiO₂ had a primary particle diameter of ca. 12 nm and a BET area of 200 ± 25 m² g⁻¹. The sample was dried for 24 h in a vacuum oven at 60 °C before the experiments.

Gemini surfactant, ethanediyl- α,ω -bis(tetradecyldimethylammonium bromide) (14-2-14), whose chemical structure is shown in Scheme 1, was synthesised in our laboratory and confirmed by ¹H NMR and elemental analysis.³⁰ Cationic surfactant, tetradecyltrimethylammonium bromide (C₁₄TABr, purity 99%) was purchased from Sigma-Aldrich Co. (USA) and used without further purification. The water used in these experiments was obtained from a Millipore water purification system, having a resistivity higher than 18.2 M Ω cm.

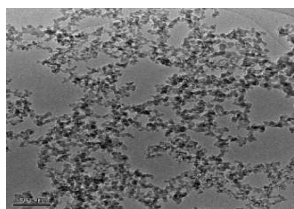
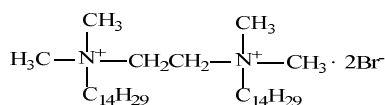


Fig. 1 TEM image of the fumed silica.



Scheme 1 Chemical structure of gemini surfactant 14-2-14.

2.2. Measurements

Foamability and foam stability measurements were made with a set-up reported in the previous issue.²⁹ The test solution of 5 mL was poured into a cylindrical glass container (25 mm internal diameter, 140 mm height) with a porous glass disc fixed at its bottom. The cylindrical glass container was put in a water bath with a constant temperature of 25 ± 0.1 °C.

The solution was bubbled by gas with a constant flow rate of 68 mL min⁻¹ and foam was generated until a designed height and then the valve was shut. Foamability was characterised by the ratio, R_v , as defined as $R_v = 20/(t \times S)$, where t is the foaming time required to reach a foam volume of 20 mL, *i.e.* a height of 40 mm in the present test, and S is the gas flow rate. Foam stability was determined from the time $t_{1/2}$ needed for the collapse of the foam to half of its initial height of 40 mm. The experiments were repeated at least three times and all presented values were the means from these replicates.

Zeta potential measurements were performed by Zeta potential analyser (Brookhaven Instrument Corporation, USA) equipped with a microprocessor unit to measure the zeta potential. Silica nanoparticles (0.05 wt%) were dispersed in aqueous surfactant solutions and the sample tubes were vibrated for 48 h in a water-bath, held at 25 °C, to reach adsorption equilibrium. The final zeta potential value was taken as an average of three measurements.

Interfacial dilational rheology was measured in an optical angle meter (OCA-20) with an oscillating drop accessory (ODG-20). The equilibrated interface as indicated by a constant surface tension value was disturbed by sinusoidal oscillations produced by a function generator, which resulted in interfacial periodic expansion and contraction. The accessible frequency range was 0.01–1 Hz and the relative area (A) variation was ϵ , ca. 6 %. These conditions followed the range of linear viscoelasticity. The changes in drop shape were monitored by CCD camera with a minimum of 50 frames per second. At the end of the experiment, the software retrieved the images and calculated the changes in both interface tension (dr) and area (dA), which gave the interface dilatational modulus $\epsilon^* = dr/dA$. Using a Fourier transform analysis, the phase angle (θ) was determined. Thus, the dilational elasticity ϵ and dilational viscosity η could be calculated as follows:

$$\epsilon = |\epsilon^*| \cos \theta \quad (1)$$

$$\eta = \frac{|\epsilon^*|}{\omega} \sin \theta \quad (2)$$

3. Results and discussion

3.1. F-SiO₂ particles modified with surfactant

In the absence of surfactant, the silica particles were negatively charged with a mean zeta potential of -22.8 mV, which made these particles disperse stably in water due to their repulsive interactions. Surface activation was carried out *in situ* via the interaction with cationic surfactant, 14-2-14 or C₁₄TABr, in water. Fig. 2 shows the variation of the zeta potential of the F-SiO₂ particles dispersed in cationic surfactant solutions. With increasing surfactant concentration, the zeta potential changed from negative to positive and the positive values continuously increased to a plateau after the *cmc*, the critical micelle concentration of surfactant in the presence of F-SiO₂ as measured by surface tension technique (Fig. S1, Supporting Information, SI). This indicated the adsorption of

cationic surfactant molecules on the particle surfaces as suggested in many cases.³¹⁻³⁴ The appearance of the solutions is shown in Fig. 3, where the silica dispersions progressed from being stable to flocculated (with sedimentation) to re-stabilised as a function of the concentration of added surfactant. For both surfactants, flocculation all appeared at zero, or low, zeta potentials as marked by solid symbols in Fig. 2, agreeing with general observations.^{33,34} These combined results described the details of surfactant adsorption: in the initial stage, cationic 14-2-14 or C₁₄TABr were adsorbed on negative F-SiO₂ particles via a Coulombic interaction, which neutralised the charge of the particles and increased the zeta potential. This formed an adsorption monolayer of cationic surfactant molecules with head-on particle configurations, and the particle surface became partly covered by the hydrocarbon chain of the adsorbed surfactant molecules. As a result, the hydrophilicity of the F-SiO₂ particles decreased and flocculation occurred. When the surfactant concentration was further increased, the adsorption continuously progressed and the second layer of surfactant formed via hydrophobic attraction with the chains of those adsorbed surfactant molecules in the monolayer, which resulted in the particles now becoming coated by a bilayer of surfactant molecules and their surface recharged, therefore, the repulsive interactions between the particles were established again and the solution returned to a clear state of appearance. A schematic for this mechanism is inserted in the middle of Fig. 3 to show the *in situ* modification by gemini surfactant.

As described above, the wettability of particles strongly depended on surfactant bulk concentration, which was consistent with general observation elsewhere.^{22, 33,34} The modification efficiencies of different surfactants can be distinguished by C₀, which was defined as the surfactant concentration making the zeta potential of particles zero. The value of C₀ was 0.021 mmol L⁻¹ for 14-2-14 and 0.81 mmol L⁻¹ for C₁₄TABr, respectively. The former was only 1/40 of the latter. This indicated that the gemini surfactant had a far higher adsorption activity than its monomer, agreeing with our previous conclusion^{29, 30} and also with other report.³⁴ Modification to F-SiO₂ particles *in situ* improved their wettability from strongly hydrophilic to partially hydrophobic, encouraging particle adsorption at the air/water interface of foams, *i.e.*, becoming a foam stabiliser. For this purpose, the gemini surfactant was evidently more efficient than its monomer surfactant.

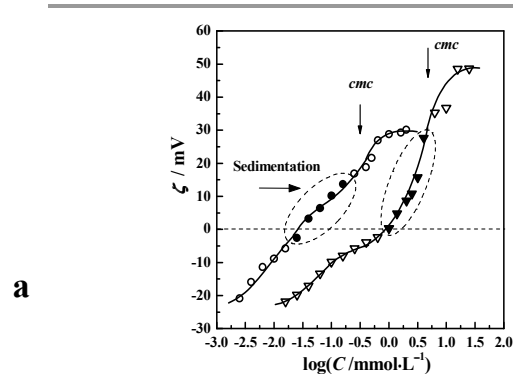


Fig. 2 Zeta potential as a function of surfactant concentration in the samples of F-SiO₂ (0.05 wt%)/14-2-14 (○) and /C₁₄TABr (▽). The solid symbols indicate the flocculation thereby.

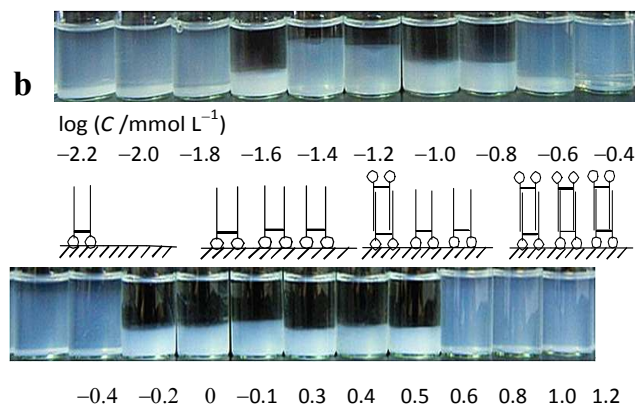


Fig. 3 Appearance of F-SiO₂ (0.05 wt%) dispersed in cationic surfactant solutions of (a) 14-2-14 and (b) C₁₄TABr with different concentrations at 25 °C. A schematic for this gemini modification mechanism is inserted in middle.

3.2. Foamability and foam stability

Fig. 4 shows semi-logarithmic plots of the foamability, represented as the ratio R_V (see the definition given in Section 2.2), against surfactant concentration, from which the maximum R_V^{\max} corresponding to the plateau and the critical surfactant concentration C_R to level out the curve can be obtained. Both quantities represent respectively the effectiveness and the efficiency of the surfactant with regards its foamability. For the present system, the values of R_V^{\max} and C_R were 3.58 and 0.383 mmol L⁻¹ for F-SiO₂/14-2-14 and 4.04 and 5.37 mmol L⁻¹ for F-SiO₂/C₁₄TABr, respectively. The C_R of F-SiO₂/14-2-14 was much lower than that of F-SiO₂/C₁₄TABr (less than 1/10 of the latter), but by comparison their R_V^{\max} values were close for each other (the former was 0.9 time the latter). This was similar to previous observations in other gemini systems,²⁹ and was also consistent with the surface tension reduction situation of gemini surfactants,³⁵ for which geminis have far higher efficiency than the corresponding monomer but do not enhance the effectiveness noticeably compared therewith. This is perhaps a characteristic of gemini surfactants relating to their interfacial adsorption behaviour and therefore also affects their foamability.

Foam stability can be characterised by the time needed for the collapse of foam to half of its initial height, $t_{1/2}$.³⁶ Fig. 5a

shows the $t_{1/2}$ of F-SiO₂/14-2-14 system as a function of surfactant bulk concentration. The value of $t_{1/2}$ rapidly increased to a maximum with increasing 14-2-14 concentration and then dropped to a minimum, following which $t_{1/2}$ re-increased and stabilised at higher concentrations. Since the maximum produced over the range of surfactant concentrations where the flocculation occurred was as seen in Fig. 3, the scenario can be described as follows: under modifying by 14-2-14, the F-SiO₂ particles became moderately hydrophobic and were adsorbed at the foam film, which stabilised the foam. When the surfactant bulk concentration increased, the adsorption on the particles continuously progressed, which returned the wettability of particles to a hydrophilic state due to the formation of adsorbed bilayers. As a result, the particles desorbed and the stability of the foam reduced rapidly. The free surfactant molecules in the bulk filled in the gaps spontaneously and the foams were re-stabilised by the surfactant alone, which could be the situation evinced by the plateau in Fig. 5a, where the identical level of the plateau for both F-SiO₂/14-2-14 and 14-2-14 alone supported this hypothesis.

As a comparison, Fig. 5b shows the variation of $t_{1/2}$ for the F-SiO₂/C₁₄TABr system, in which a similar image is also shown: $t_{1/2}$ increased rapidly and reached a maximum with increasing C₁₄TABr concentration, and then decreased to a plateau identical to that with C₁₄TABr alone. Similar results supported the above mechanism of foam stability generation by mixed surfactant and F-SiO₂ particles.

Comparatively, the maximum $t_{1/2, \max}$ of F-SiO₂/14-2-14 (2490 min) was *ca.* seven times higher than that of F-SiO₂/C₁₄TABr (357 min). Moreover, the surfactant concentration C_p yielding the maximum was 0.063 mmol L⁻¹ for F-SiO₂/14-2-14 and 3.51 mmol L⁻¹ for F-SiO₂/C₁₄TABr, respectively. The former was only 1/50 of the latter. These all indicated that the gemini surfactant was much better, and more efficient, than the traditional surfactant in helping F-SiO₂ to stabilise foams.

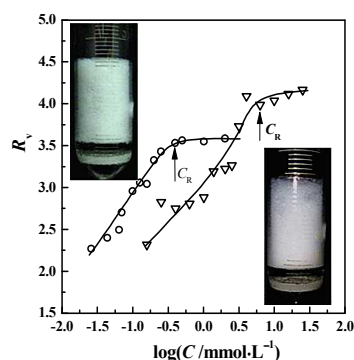


Fig. 4 Semi-logarithmic plots of foamability (R_v) of a mixed F-SiO₂ (0.05 wt%)/14-2-14 (○) and /C₁₄TABr (▽) system against surfactant concentration at 25 °C.

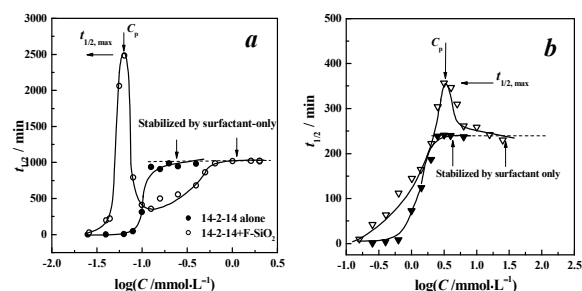


Fig. 5 Semi-logarithmic plots of foam stability ($t_{1/2}$) against surfactant concentration for 14-2-14 (a) and C₁₄TABr (b) at 25 °C. Open and solid symbols correspond respectively to mixed particles (0.05 wt%)/surfactant and surfactant only.

3.3. Visco-elastic properties of the adsorption films

Generally, highly stable foam is related to highly visco-elastic foam film.^{37,38} In this section, the visco-elastic properties of the adsorption films generated by F-SiO₂/14-2-14 were studied. Fig. 6 shows the experimental plots of dilational elasticity ε and dilational viscosity η against the frequency of sinusoidal oscillation. For comparison, the films generated by surfactant alone were also studied. Both ε and η all showed pronounced frequency-dependence. Increasing disturbance frequencies meant a decrease in respond time, over which the particle/surfactant exchanged between the interface and the bulk, and also moved inside the monolayer to restore equilibrium. At low frequencies, the time for particle/surfactant response was sufficient and thus various relaxation processes arose from both diffusion and adsorption³⁹ and/or arrangement changes of adsorbed particles/molecules⁴⁰ can occur. At high frequencies, the monolayer had no time to respond and behaved as if it were an insoluble film.

Furthermore, the bulk concentration of the surfactant also affected the interfacial rheology. Fig. 7 shows the concentration-dependence of ε , similar plots for η are available in Fig. S2, SI. At a fixed frequency, the experimental ε passed through a maximum with increasing surfactant bulk concentration. For systems with surfactant alone, the maximum was a common phenomenon.^{29,30,41,42} It has been explained in two ways:⁴¹ one was to increase the interface excess Γ with increasing bulk concentration, which led to a higher elasticity, and the other was to accelerate the molecular exchange between bulk and interface, which can rapidly balance the interface tension gradient dy and resulted in $\varepsilon = 0$. Thus, at low concentrations the increase in ε was dominant, whereas at high concentrations ε decreased since the molecular exchange was accelerated, resulting in a maximum appearing in the ε versus C curve. In the present system, similar results were also obtained, which indicated that the hydrophobic particles were analogous to amphiphilic surfactants in many respects when they were used as foam stabilisers.⁹ However, the situation in the presence of particles was often more complicated,^{25,43,44} for example, two maxima appeared in the gemini case (Fig. 7a).

According to the discussion for Fig. 5a in Section 3.2, the two maxima in Fig. 7a can be attributed to the adsorption films consisting of the particles together with 14-2-14 and of 14-2-14 alone, respectively. Around the first maximum, the adsorption of the F-SiO₂ particles was favourable since the surfactants at corresponding concentrations made them partly hydrophobic. At the second maximum, however, the particles became hydrophilic once again due to their surface being covered by the adsorbed surfactant bilayers and thereby the particles desorbed from the foam films: only surfactant molecules remained. The present result showed the complexity of the system when the solid particles, modified *in situ*, were used as foam stabilisers. For achieving highly stable foams, the surfactant concentration should be designed with this in mind.

The maximum elasticity corresponding to the first peak in Fig. 7a had a value of 354 mN m⁻¹ at 1 Hz, which was considerably higher than that at the second peak (214 mN m⁻¹). This indicated that the film consisting of the solid particles had stronger elasticity than that with the surfactant alone.

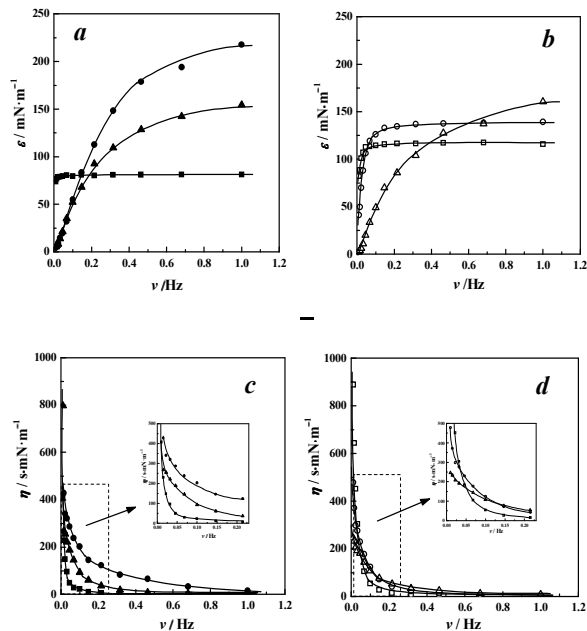


Fig. 6 The experimental plots of interfacial dilational elasticity (ϵ) for F-SiO₂/14-2-14 (a) and 14-2-14 only (b), and dilational viscosity (η) for F-SiO₂/14-2-14 (c) and 14-2-14 (d) as a function of frequency (ν) at 25 °C. The symbols represent different surfactant concentrations: $\log(C / \text{mmol L}^{-1}) = -1.40$ (squares), -1.20 (circles), -0.50 (triangles).

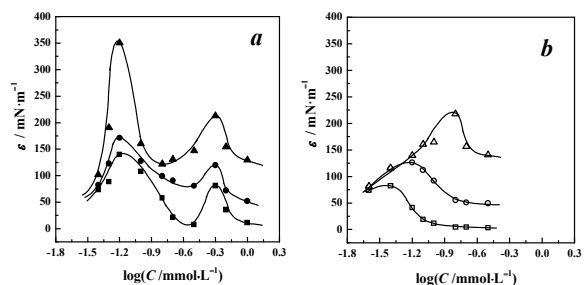


Fig. 7 Semi-logarithmic plots of interfacial dilational elasticity (ϵ) for F-SiO₂/14-2-14 (a) and 14-2-14 alone (b) as a function of 14-2-14 concentration at 25 °C. Symbols representation: $\nu/\text{Hz} = 0.01$ (squares), 0.10 (circles), and 1.00 (triangles)

3.4. Interfacial elasticity and foam stability

For surfactant-stabilised foams, the elasticity of the adsorption film was believed to be a dominant factor affecting foam stability.^{29, 30, 37, 41, 45-47} High elasticity generally corresponded to high foam stability. Fig. 8 shows a comparison of the elasticity generated by the particle-adsorbed film and the stability of the corresponding foam: both were consistent, *i.e.*, highly elastic particle films were mirrored in their highly stable foams. This result was consistent with the observation made by Stocco *et al.*,²⁶ again stressing a possible natural characteristic for foam stability.

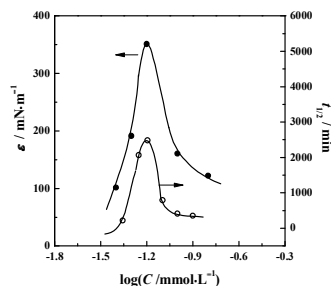


Fig. 8 Comparison of interfacial elasticity (ϵ) and foam stability presented as $t_{1/2}$ for F-SiO₂/14-2-14 at 25 °C

4. Conclusions

Herein, we report on highly stable aqueous foams generated by fumed silica particles hydrophobised *in situ* with a quaternary ammonium gemini surfactant. The following conclusions were obtained:

- (1) The commercially available fumed silica was an excellent stabiliser for aqueous foams when these particles were hydrophobised *in situ* with a quaternary ammonium gemini surfactant, 14-2-14.
- (2) Both the ability and efficiency of 14-2-14 in modifying F-SiO₂ were far higher than those of the corresponding monomer C₁₄TABr, showing the advantage of the gemini structure of surfactant.
- (3) For the system where the solid particles were *in situ* hydrophobised with a surfactant, there were the synergism and competition between the particles and the free surfactant

molecules for their adsorption at the foam film. Therefore, the bulk concentration of surfactant should be carefully designed so as to play the optimal effect of the particles.

(4) The foam stability when stabilised by solid particles was mirrored in the elasticity of its film. Highly elastic film favoured the generation of highly stable foams.

Acknowledgment

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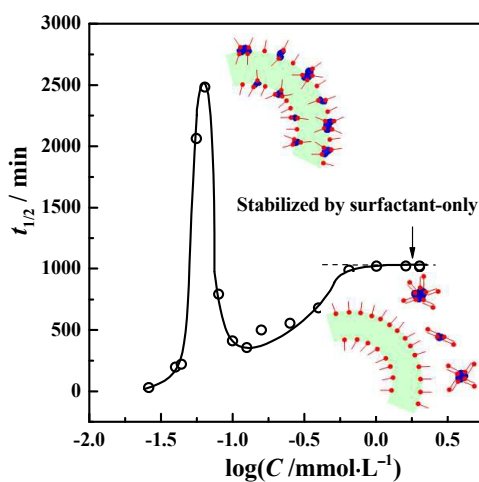
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Graphical abstract

Highly stable aqueous foams generated by fumed silica particles hydrophobised *in situ* with a quaternary ammonium gemini surfactant†

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Fumed silica hydrophobised *in situ* with a quaternary ammonium gemini surfactant was an excellent stabiliser for aqueous foams.