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ARTICLE TYPE

Mixtures of latex particles and surfactant of opposite charge used as interface stabilizers-

Influence of particle contact angle, zeta potential, flocculation and shear energy

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Abstract

We investigate the stabilization of air-water interfaces by mixtures of negatively charged latex particles (sulfate polystyrene) and cationic surfactants (alkyl trimethylammonium Bromides). First we report results concerning the binding of surfactant molecules to the latex particles. As the surfactant concentration increases, the charge of the particles reverses, from negative to positive, because the C_nTAB first bind electrostatically to the latex particles and then through hydrophobic interaction with the monolayer already adsorbed on the particles as well as directly with the hydrophobic surface of the latex. Over a large range of surfactant concentrations around the charge inversion, a strong flocculation is observed and 100µm large aggregates form in the suspension. Unlike previous studies published on mixtures of inorganic particles with oppositely charged surfactants, we show that we can vary the sign of the zeta potential of the particles without changing the contact angle of the particles over a large range of surfactant concentrations. Indeed, the latex particles that we study are more hydrophobic than inorganic particles, hence adding moderate concentrations of surfactant results in a weak variation of the contact angle while the charge of the particles can be reversed. This enables to decouple the effect of zeta potential and contact angle on the interfacial properties of the mixtures. Our study shows that the contact angle and the charge of the particles are not sufficient parameters to control the foam properties, the key-parameters are the flocculation state and the shear energy applied to produce the foam. Indeed, flocculated samples, whatever the sign of the zeta potential, enable to produce a stable armour at the interface. The large aggregates do not adsorb spontaneously at the interface because of their large size, however when a large shear energy is used to produce the foams very stable foams are obtained, where particles are trapped at interfaces. We suggest that the large aggregates may be broken during the shear and may reform at the interface to form a solid armour. A simple calculation taking into account the adsorption dynamics of the aggregates as a function of their size is consistent with this hypothesis.

A Introduction

Colloidal particles adsorbed to liquid interfaces provide unique properties to the interface in comparison to standard surfactants.[1–3] Unlike standard surfactants, colloidal particles adsorb irreversibly to interfaces and form a solid armor at the interface, whose mechanical properties has been studied by several research groups.[4–12] It is known that such colloidal armor is very stable upon compression[13–15], leading to the outstanding stability of particle-stabilized foams and emulsions against Ostwald ripening[16]. Solid particles also provide a mechanical protection which is useful to produce liquid marbles[17,18] or 'water powder'.[19,20] The desorption energy of the particles depends critically on the hydrophobicity of the particles, which is quantified by the contact angle, θ, made between the particle surface and the fluid-fluid interface. For a given particle radius R, the desorption energy, which scales as[21] $\Delta G \approx R^2\gamma(1\pm\cos\theta)^2$, with γ the liquid/liquid or liquid/air interfacial tension, is maximal for $\theta=90°$. However, when particles are too hydrophilic ($\theta \sim 0°$) or too hydrophobic ($\theta \sim 180°$) the desorption energy tends toward zero and as a result such particles are usually not efficient at stabilizing the interface. In the literature, one can find several ways to control the contact angle of the particles, for example by using hydrophilic particles such as silica or glass particles, which are hydrophobized by chemically grafting a hydrophobic group at the interface, such as a silane group.[3,22–24] Another strategy, known as 'in-situ hydrophobization', consists in mixing inorganic particles, such as $CaCO_3$[25], Laponite[26, 27] or silica[28-30] with oppositely charged surfactants. For surfactant concentrations well below the CMC, the heads of the surfactants bind to the surface of the particles through electrostatic interaction and form a monolayer with their hydrophobic tail in contact with the water. As the concentration increases, the particles undergo a charge reversal, as the surfactant molecules form a bilayer on the particles. The charge of the particles is also known to be a crucial parameter : positively charged particles tend to stabilize interfaces better than negatively charged particles[1], presumably because anionic particles are repelled by the electric charge of the bare fluid-fluid interface, which is negative.

The most stable foams are obtained for surfactant concentrations around the charge inversion and where the contact angle is the largest, usually between 50 and 90°[25–30]. These studies show that the addition of surfactant enables to modify both the charge and the contact angle of the particles, however it is difficult to decouple both effects.

In contrast to inorganic particles, there are fewer studies reporting the use of latex particles to stabilize interfaces although such particles have the advantage of having a much more controlled size and have a much lower density, which is an advantage to produce low density materials for energy-saving issues[31]. It has been shown that the charge of latex particles is crucial : anionic latex do not stabilize foams whereas cationic latex do[32]. In a study of Binks *et al*. it was found that in conditions of low pH, solutions containing carboxylic acid latexes produced foam while at high pH, no foam could be produced[33]. However for latex particles, the role of the contact angle on the foam properties was not investigated.

We study mixtures of anionic polystyrene latex and a series of C_nTABs, a cationic surfactant. We show that we can vary the sign of the zeta potential independently without changing the contact angle over a large range of surfactant concentrations. Indeed, the latex particles that we study are more hydrophobic than inorganic particles, hence adding moderate concentrations of surfactant results in a weak variation of the contact angle while the charge of the particles can be reversed.

Our study shows that a contact angle of 90° is not sufficient to stabilize the foams and that the sign of the zeta potential is not correlated to the foam stability. The key-parameters are the flocculation state of the suspension and the shear energy applied to produce the foam. Flocculated particles, whatever their charge, enable to produce a stable armour at the interface. However the aggregates do not spontaneously adsorb to interfaces and a large shear energy energy is needed to produce the foams. We suggest that the aggregates may be broken in the shear which enables a faster adsorption at the interface.

B Materials and methods

Materials.

Monodisperse surfactant-free latex particles (polystyrene microspheres of 0.10µm diameter, electrostatically stabilized by sulfate surface groups) were purchased from Interfacial Dynamics Corparation IDC now owned by Invitrogen®, as aqueous dispersion containing 8 wt% particles. The charge density is 1.3 $\mu C/cm^2$. A TEM image of the particles can be found in SI.

Dodecyltrimethyl ammonium Bromide, $C_{12}TAB$ (CMC=15 mmol/L), Tetradecyltrimethyl ammonium Bromide, $C_{14}TAB$ (CMC=4.5mmol/L), and Hexadecyltrimethyl ammnonium Bromide, $C_{16}TAB$ (CMC=1 mmol/L), were purchased from Aldrich with a purity of 98 % or more and used without additional purification.

Preparation and characterization of particle-surfactant mixtures.

Aqueous mixtures of particles (2.5 wt%) and surfactant (concentration C_s) were prepared by mixing 3mL of a 5.0 wt% particle suspension and 3mL of a surfactant solution of concentration $2C_s$. The resulting solutions have therefore a volume of 6mL, a particle concentration of 2.5 wt% and a surfactant concentration of C_s. The surfactant solution was added to the particle suspension dropwise and under moderate agitation (magnetic stirring) to avoid particles to meet local high surfactant concentration. The samples were then allowed to equilibrate 24h under moderate agitation.

To illustrate the phase-diagram, we present photographs of the equilibrated vessels after shaking the samples (Figure 2). In the case of the flocculated solutions, the aggregates can be clearly observed as they adhere to the glass of the vessels.

The Zeta potential of the particles were calculated from the electrophoretic mobilities measured by a Malvern Zetasizer Nano Series ZS90 instrument, using the Hückel model equation[34]. The samples used for this measurement were 250-fold diluted in milli-Q water to reach a particle concentration of 0.01 wt% and avoid multiple scattering of light. At least 3 measurements were made for each sample. We are aware that the dilution may induce a desorption of the surfactant from the particles, especially for the less hydrophobic surfactants. Actually this was probably the case when we used C_6TAB a surfactant which is poorly hydrophobic (data not shown) where we never observed charge inversion. However we observed charge inversion for the three systems, C_{12}, C_{14}, $C_{16}TAB$ meaning that hydrophobic interaction seem to be strong enough to prevent large desorption.

Measurement of free surfactant and surfactant adsorption isotherm on the particles

TOC, Total Organic Content, measurements (Shimadzu-VCSH) enable to obtain the amount of carbon in the solutions, from which we can deduce the concentration of free surfactant in the solutions hence the amount of adsorbed molecules on the particles.

2mL of equilibrated particle-surfacant mixtures was ultracentrifuged at 45 000 rpm for 60min (Beckman Coulter OptimaMAX Ultracentrifuge). Then 1.2mL of supernatent was taken and ultracentrifuged again at 45000 rpm for 60min. 1mL of supernatent was then placed into a glass vessel, and 10-fold diluted in Milli-Q water, to be analyzed by a Total Organic Carbon analyser. The amount of Non Purgeable Organic Carbon (NPOC, given in mg/L) in the sample measured by the instrument is then converted into the molar concentration of free surfactant there originally present in the supernatent. The surface coverage of the particle by the surfactant, Γ, was then calculated by $\Gamma = (C_{s0} - C_{sTOC}) / (C_pS_p)$ where C_{s0} is the initial surfactant concentration in the sample, C_{sTOC} is the concentration of free surfactant determined by TOC measurement, C_p the particle concentration, and S_p the area of one latex particle. The dotted line drawn in Figure 3 represents the surface coverage which would be measured if all the surfactant molecules bind to the particles, it writes, c_{s0}/c_Ps_P.

Thin film observation.

The stability of freely suspended films and the ability of the particles to spontaneously adsorb in the film was obtained using a home-made thin-film balance apparatus, described in Claesson *et al*.[32] A Scheludko cell is used to form a horizontal thin-liquid of solution.[33] The film is placed in a chamber in which we can fix the pressure. This cell is placed under a microscope (Olympus BX51WI) and observed with white light interference. The analysis of the reflected Newton colours enables to determine the thickness of the films as they drain. Pictures were captured by a video camera.

Preparation and characterization of foams.

The 6mL particles-surfactants mixtures contained in 20 mL glass vessels were foamed using an rotor-stator mixer (IKA T25 digital Ultra-turrax) at maximal speed of 24 000rpm for 30s. Resulting mixed samples were stored at room temperature over 15 days.

For samples whose foam remained stable over 24 h, a small amount of foam was taken and carefully placed on a glass wafer to be observed with an optical microscope (Olympus BX51WI) equiped with a camera.

Measurement of the contact angle at equilibrium

To measure the contact angle of the particles with the air-water interface, a 5 µL drop is deposited on a coating made from the latex particles prepared as follows. 1 mL of suspension is left to dry at air until most water was removed. The resulting partially wet powder was recovered to coat a glass wafer with a thin layer of particles, using a spatula to get a homogeneous layer, and dried in an air oven at 40 °C for 24 h. Then the measurement consists in depositing a 5 µL water droplet on the latex layer with a micropipet and capture a side photograph of the droplet. The contact angle is then determined using the ImageJ software. In the case of solutions where surfactant is in excess, we centrifuge the samples 2 times and remove the supernatent so as to prepare a latex powder without free surfactant. The coating can also be prepared by spincoating to obtain a more homogenous coating (see SI). The contact angle obtained after spin coating is usually 10-15° lower than the one obtained with the previous method but remains above 90°.

C. Results

1. Interaction between anionic latex particles and a series of C_{12}TAB, C_{14}TAB and C_{16}TAB. We use zeta potential measurements as well as Total Organic Content. Zeta potential is related to the surface potential of the particles and the TOC enables to obtain the concentration of free surfactant in the solution. In Figure 1 we find that for the three surfactants, the zeta potential of the particles goes from a negative value (-100 mV) at low surfactant concentration to a positive value (+100 mV) at high surfactant concentration, similarly to what was measured by Connor et al.[37] for latex particles. Indeed, the cationic surfactants firstly bind to the negatively charged sulfate groups of the latex particle, reducing the negative charge of the latex particles. Above a concentration of the order of 0.3 to 0.5 mM the additional surfactant molecules bind through hydrophobic interaction either to the first surfactant molecules

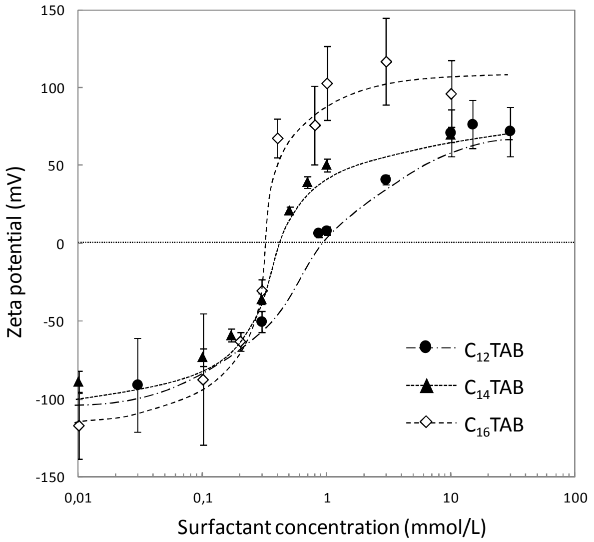


Fig. 1 Evolution of zeta potential of aqueous latex particles dispersions (2.5 wt%) with initial concentration of surfactant (dashed lines guide the eye).

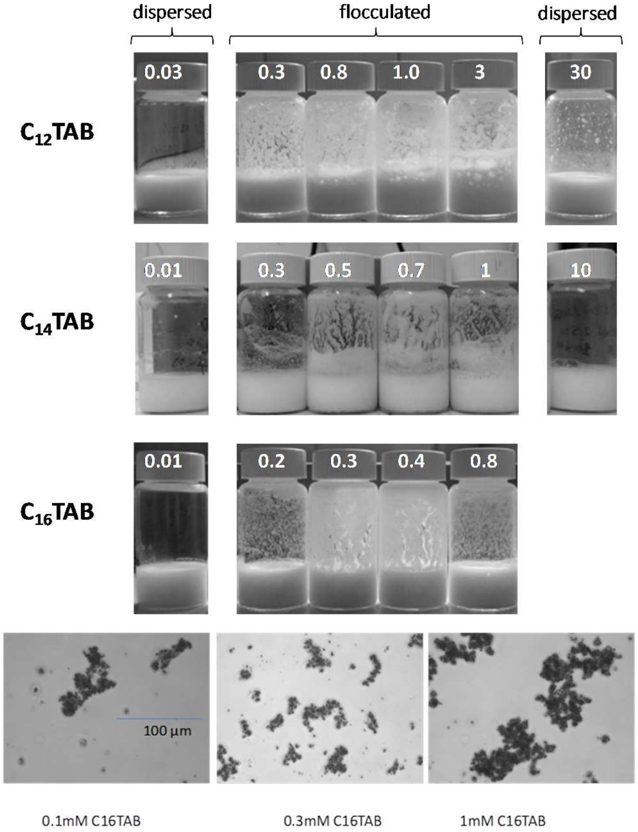


Fig. 2 Top. Photographs of vessels containing 6mL of aqueous latex particle dispersion (2.5 wt%) as a function of surfactant concentration (given in mM above the vessels). After shaking the samples, observing the walls of the vessels, where the aggregates remain, enable to obtain qualitative information about the flocculation. Bottom Optical micrographs of the aggregates obtained in various conditions. In the flocculation zone, the size of the aggregates is of the order of 100 µm

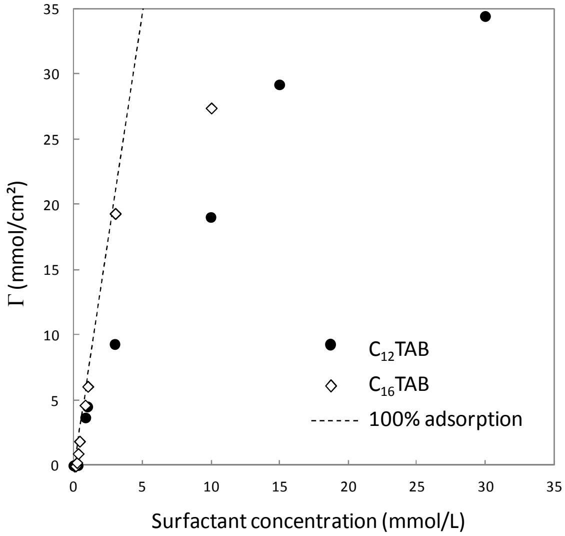


Fig. 3 Amount of adsorbed surfactant on the particles as a function of initial surfactant concentration for aqueous latex particle dispersions (2.5 wt%). Dashed line represents the limit case where 100% of the surfactant is adsorbed on the particles.

bound to the latex surface or directly to the hydrophobic surface of the latex as shown by Connor *et al.*[37] It is also known that cationic hemimicelles can form on anionic particles leading to a large positive value of the zeta potential.[38,39]
Between 0.3 and 2 mM where the particles become uncharged, the sample flocculate strongly (Figure 2), forming large aggregates of the order of 100 µm. It should be noted that the flocculation is observed even for positive and negative zeta potentials probably because of strong Van der Waals forces; For larger surfactant concentrations, the particles are well dispersed.
Figure 3 presents the TOC results, from which we obtain the surface excess of C_nTAB adsorbed on the latex particles. The dotted line represents the theoretical surface excess Γ which would be measured if all surfactants molecules were adsorbed on the particles. We find that below 3 mM for $C_{16}TAB$ and 1 mM for $C_{12}TAB$, there is no excess of surfactant in the solution meaning that all surfactant molecules bind to the latex particles, and above these concentrations free surfactant can be found in the solution. It should be noted that the results are very similar to the ones presented by Connor et al for latex particles[37].

We measured the contact angle of the latex particles by depositing water droplets on a glass slide coated with the particles suspensions (Figure 4). We find that the particles are hydrophobic (contact angle of the order of 120°) for $C_{16}TAB$ concentrations between 0.01 and 1 mM. We note that the values of the contact angle may be overestimated because of the rugosity of the coating, which is larger that the rugosity of the particles but that it can only make an hydrophobic surface ($\Theta > 90°$) more hydrophobic. So the surfaces with an apparent contact angle around 120° certainly have a real contact angle around 100° but not smaller that 90°. Then, the contact angle is close to the optimum to stabilize foams. Also, it does not alter the comparison between the particles.

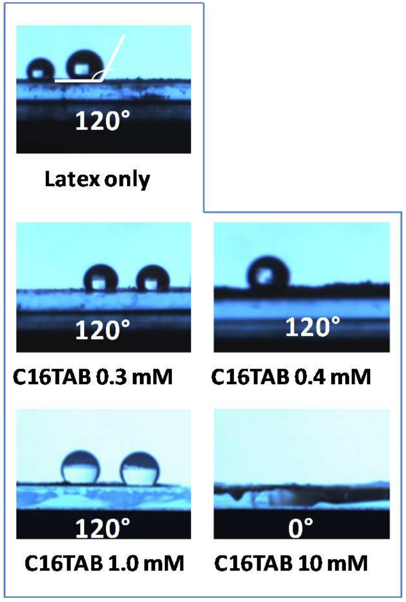


Fig. 4 Determination of particle contact angle for different $C_{16}TAB$ surfactant concentrations.

Above 10 mM, the contact angles becomes close to zero, as the water droplets penetrate into the powder coating when they are deposited. We are quite surprised by this result as we expected a similar contact angle for the samples having an absolute value of the zeta potential equal to +100 mV, between 1 and 10 mM surfactant. Values of zeta potential are obtained from a mobility measurement and the value of the zeta potential depends on the model which is used and also on the slipping plane. The slipping plane, which depends on the hydrophobicity, may not be the same for all samples, which could explain this surprising result. Although the absolute zeta potential is equal, we suggest that the surface density of $C_{16}TAB$ heads is very large at high concentration, because not only the cationic surfactant can either form a bilayer for each initial sulfate group but additional cationic charges are also brought by the direct adsorption of C_nTAB tails by hydrophobic interactions on the latex surface.

Conclusion on interactions between surfactant and particles- Similarities and differences between latex and inorganic particles.
Similarly to inorganic/surfactant systems, our latex/surfactant particles undergo a charge reversal upon addition of surfactants. However, as polystyrene is more hydrophobic than silica or other inorganic particles, the contact angle is above 90° even in the absence of surfactant. Hence adding moderate amounts of surfactants results in a variation of the charge of the particles but the contact angle remains constant. Our system therefore enables to decouple the influence of the contact angle and electric charge on the interfacial properties, which is the object of the next section.

Interfacial behaviour. We first study the thin-liquid films prepared from these mixtures. As illustrated in Figure 5, we find that the latex particles are never trapped in the films for any of the samples studied, unlike in Velikov *et al.*[40] Indeed the drainage of the liquid is fast – a few seconds – for all the studied samples independently of the concentration and hydrophobicity of the surfactant. The Newton colours corresponding to our 100 nm

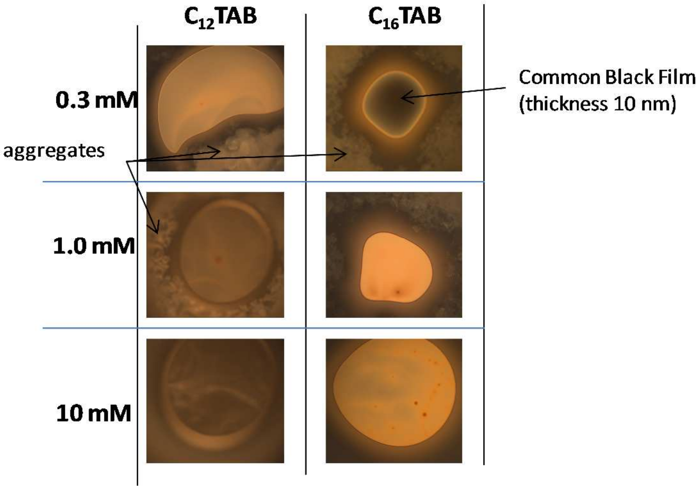


Fig. 5 Photographs of thin films of latex particle dispersions (2.5 wt%) as a function of surfactant concentration, observed with the thin-film balance apparatus. The photos represent a zone of width 200 µm. Large aggregates (arrows) are expelled from the thin-films to the meniscus, known as the Plateau border.

latex particles would be blue and therefore easy to identify. Instead, the reflected colour is grey corresponding to a Common Black films, which thickness is of the order of 10 nm. This is much smaller than the diameter of the particles and corresponds to a film stabilized by two layers of surfactants and containing water between the two air-water interfaces.

In the case of the flocculated samples, obtained for surfactant concentrations between 0.1 and 1 mM, large aggregates (arrow) are pushed out of the film during drainage and accumulate in the Plateau borders as shown in Figure 5.

From this study of thin-liquid films, we conclude that the latex particles cannot be trapped in the films, whatever their charge, contact angle or flocculation state.

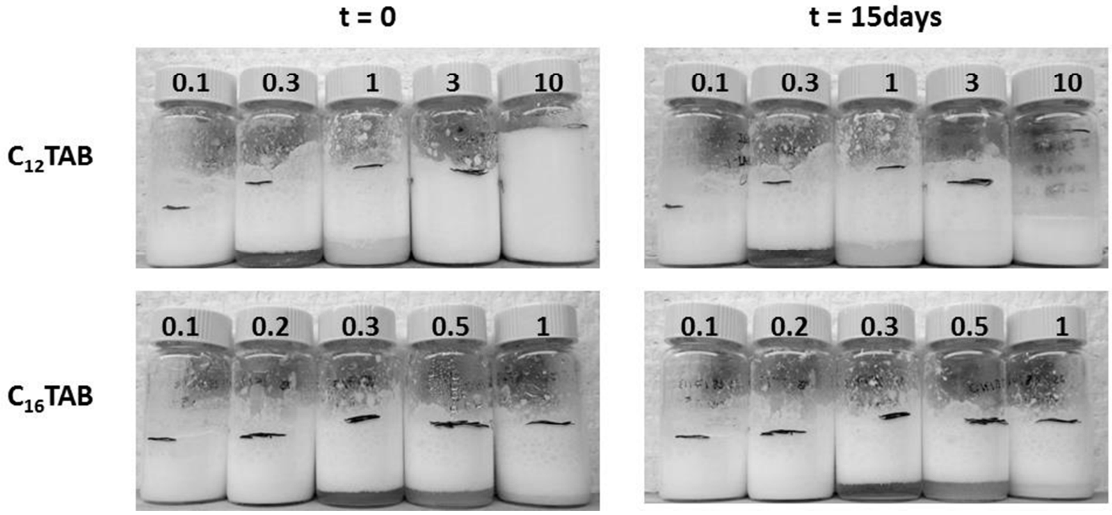
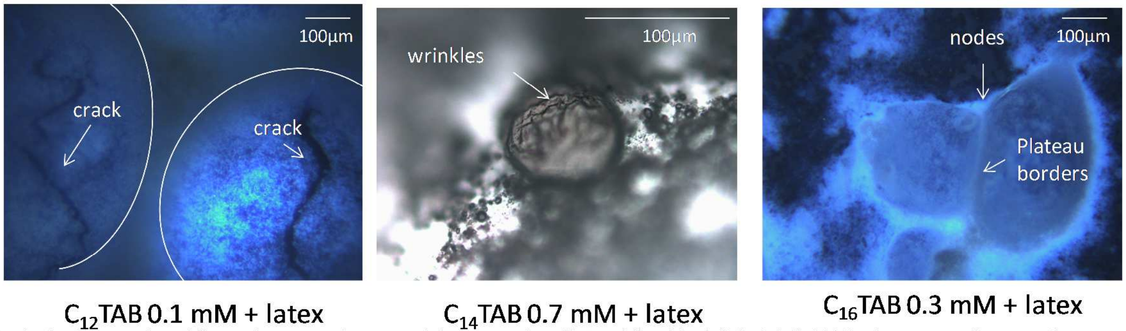


Fig. 6 Photographs of vessels containing foamed aqueous latex particle dispersion (2.5 wt%) just after foaming with rotor stator mixer (left column) and after 15 days (right column) as a function of $C_{12}TAB$ (upper line) or $C_{16}TAB$ (lower line) surfactant concentration (given in mmol/L above the vessels). Black line on the vessels merely shows the initial foam volume.



$C_{12}TAB$ 0.1 mM + latex $C_{14}TAB$ 0.7 mM + latex $C_{16}TAB$ 0.3 mM + latex

Fig. 7 Optical micrographs of foamed aqueous latex particle suspension (2.5 wt%) with a) 0.1mM $C_{12}TAB$, the arrows show cracks at the bubble surface, the circles represent bubbles b) 0.7mM $C_{14}TAB$, the arrows show wrinkles of the particle layer at the air-water interface, and c) 0.3mM $C_{16}TAB$, one can observe two bubbles connected by Plateau borders and node. One can see accumulation of latex in these zones and also particles at the surface of the bubbles.

Finally we investigate the possibility to prepare foams with these suspensions of oppositely charged latex and surfactants. We first try to obtain a foam by simply shaking the samples by hand and compare to the solutions containing the surfactant alone. For the surfactants solution, we are able to produce foams –stable for less than 3 hours, see SI- while we do not observe any foam with the latex/surfactant mixtures except at high surfactant concentration (around 10 mM for $C_{16}TAB$) where surfactant is largely in excess and above the CMC. The foam which is formed at this high surfactant concentration is stabilized by the free surfactant which adsorbs quickly at the interface. In this case, the foam is stable only over 3 hours, similarly to foams made from surfactant solutions alone. To obtain stable foams over a larger range of concentrations, we used a rotor-stator mixer, known as Ultra-turrax.

As shown in Figure 6, we find that for concentrations between 0.1 and 3 mM for $C_{12}TAB$ (0.1 and 1 mM for C_{14} and $C_{16}TAB$) , approximately 5 cm^3 of foam can be produced from an initial volume of 6 cm^3 of solution. The corresponding foams are stable over 15 days. In comparison, the foams made with the surfactant alone at the same concentrations were not stable for more than 3 hours whatever the concentration for all C_nTABs n=12-16. Interestingly, the most stable foams are obtained in the flocculation region for negatively and positively charged particles. In most of these cases, there is very little surfactant in excess –below 0.1 mM for the $C_{16}TAB$ and 0.5 mM for the $C_{12}TAB$- except for the solution containing 3 mM of $C_{12}TAB$.

Using an optical microscope we observe the surface of the bubbles from these stable foams and clearly find that colloids are adsorbed at the surface of the bubbles for the three surfactants (Figure 7 a, b, c). We have chosen these three figures to illustrate several features which are very similar to other particle-stabilized foams. In Fig 7a, a fracture can be seen at the interface (arrow), and in Fig 7b, a the interface is buckling : fractures[26,41] and buckling[5,8,22,42] were observed for other types of particle-stabilized interfaces and illustrate the solid-like behaviour of the interface. Fig 7c shows that aggreates made of latex particles also accumulate in the Plateau borders.

D. Discussion on the influence of contact angle, charge, flocculation and shear energy

To summarize, our latex/surfactant particles undergo a charge reversal upon addition of surfactants and aggregate strongly over a large range of concentrations around the charge inversion. 100µm large aggregates are formed, which are positively or negatively charged. We find that the particles can not attach to the interface when the applied shear energy is not sufficient, in the thin-film experiment or upon foaming experiments by hand-shaking, whatever the charge or contact angle of the particles. When the foaming process involves a higher shear energy (ultra-turrax), a very stable foam can be produced for the flocculated samples, whatever their charge. At higher surfactant concentration, when surfactant is in excess, a large volume of foam can be produced but its stability is not improved with respect to surfactant solutions alone- see Table 1. Below we rationalize these data to understand the influence of the contact angle and charge of the particles, shear energy and flocculation on the interfacial properties.

Conc mM	0.01	0.1	0.2	0.3	0.4	1	10
Zeta potential (mV)	-100	-100	-60	-60	+60	+100	+100
Flocculation	No	yes	yes	yes	yes	yes	no
Contact angle	100-120	100-120	100-120	100-120	100-120	100-120	0
Foam	No	Yes	Yes	Yes	Yes	Yes	Yes
Stability		15 days	15 days	15 days	15 days	15 days	3 hours

Table 1. Summary of the findings for C_{16}TAB/latex

In the intermediate range of concentrations between 0.1 and 1mM, stable foams are observed for flocculated samples where the particles are either positively or negatively charged. Hence the zeta potential does not seem to be the key parameter but rather the fact that the latex particles adsorb in agregates and probably form a percolated network at the interface[19]. In addition, we note that the mixtures with surfactant concentrations 0.01 mM and 0.1 mM present a similar zeta potential and a contact angle above 90°, however the flocculated sample – concentration 0.1 mM- enables to produce a stable foam whereas the well-dispersed sample -0.01 mM- does not foam even with a large shear energy. Again, it is needed to strongly shear the interface to adsorb the aggregates at the surface of the bubbles, otherwise they are ejected in the Plateau borders and do not make a stable foam as shown by the thin-film study. Langevin's group found that more fumed silica particles could be adsorbed at the air-water when solutions are sonicated than when the particles are left to adsorb spontaneously. The authors suggested a possible adsorption barrier preventing adsorption[43]. Instead, we suggest that the aggregates may also be broken by the sonication or the shear. Smaller aggregates probably adsorb more easily at the interface. Indeed as in the review of Tcholakova et al.[1], we introduce a typical time for adsorption, t_A and a typical time for interface creation, t_{CR}. Particles can adsorb if $t_A \ll t_{Cr}$. Both times depend on the shear energy but the ratio does not. The ratio t_A/t_{CR} scales as a/d, a being the diameter of the particles and d the size of the bubbles. For the large aggregates, of the order of 100 µm, t_A/t_{CR} =10 meaning that large aggregates cannot adsorb at the interface. However for 1 µm large aggregates or 100 nm particles t_A/t_{CR} is 0.1 and 0.01 respectively, meaning that they can adsorb. Hence we suggest that a large shear energy may help breaking the large aggregates into smaller pieces which would adsorb more easily at interfaces. Once at the interface, the aggregates may quickly reassemble because of Van der Waals and capillary interactions resulting in a solid armour protecting the bubbles against coalescence and Ostwald ripening. Using an optical microsocope we observed the aggregates before and after applying a strong shear (either ultra-sound or ultra-turrax) but we did not find a significant decrease of their size. However, the aggregates probably aggregates very quickly after stopping the shear because of Van der Waals forces.

Finally at high surfactant concentrations, a foam is obtained but its stability is that of a standard surfactant. The free surfactant in excess stabilizes the foam and the positively charged latex particles are probably too hydrophilic to adsorb at the interface.

E. Conclusion

We have investigated the stabilization of air-water interfaces by mixtures of negatively charged latex particles (sulfate polystyrene) and cationic surfactants (alkyl trimethylammonium Bromides). Our oppositely charged latex/surfactant system presents several differences with respect to previously published studies on inorganic particles/surfactant mixtures because of the fact that the surface of the particles is intrinsically more hydrophobic than that of inorganic particles.

The contact angle of the particles with the air-water interface is large even for the bare particles, hence adding reasonable amounts of surfactants enables to vary the charge of the particles without varying the contact angle. This enables to decorrelate the effect of charge and contact angle of the particles.

Our study shows that having a contact angle close to 90°, usually thought as being the optimum value, is not sufficient to stabilize the foams. Furthermore, the charge of the particles is not correlated to the foam stability. We find that the key-parameters are the flocculation state of the suspension and the shear energy applied to produce the foam. Indeed, flocculated samples, whatever the sign of the zeta potential, enable to produce stable foams, where the particles are trapped at the surface of the bubbles. However the 100 µm large aggregates do not adsorb spontaneously at the interface because of their large size. The stable foams are only obtained when a large shear energy is used to produce the bubbles. We suggest that the large aggregates may be broken during the shear and may reform at the interface to form a solid armour. A simple calculation taking into account the adsorption dynamics of the aggregates as a function of their size is consistent with this hypothesis.

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Notes and references

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