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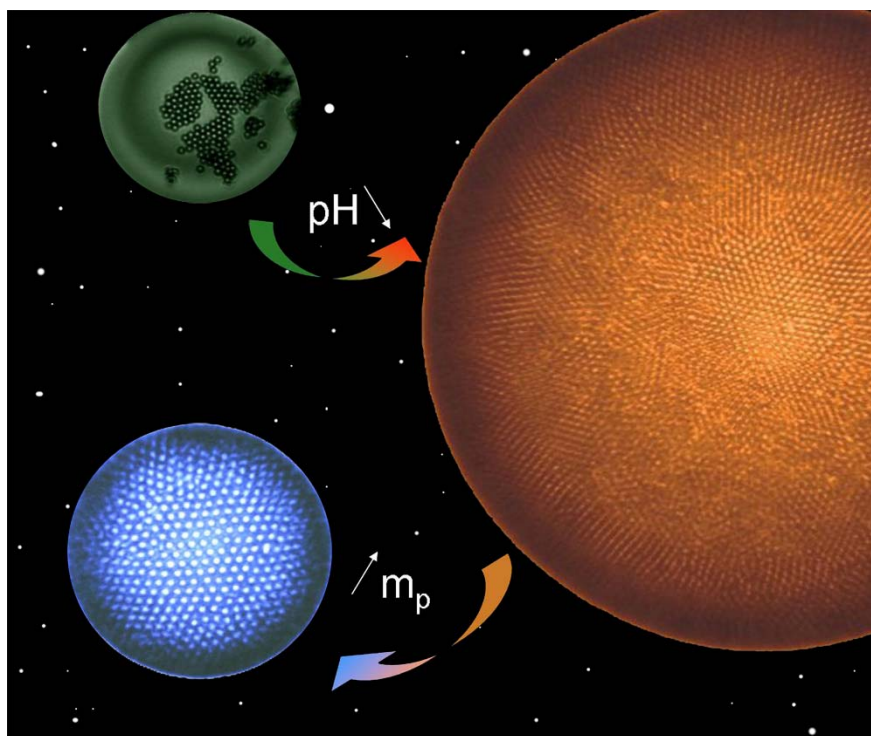
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The effect of double-chain surfactants on armored bubbles: a surfactant-controlled route to colloidosomes†‡

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We find that the gas phases of air bubbles covered with anionic or cationic polystyrene latex particles dissolve on exposure to cationic and catanionic surfactants. The particles on the bubble interface are released as singlets or aggregates when the surfactant has a single hydrophobic chain, while porous colloidal capsules (colloidosomes) with the same aqueous phase inside as out are obtained when the surfactant has two hydrophobic chains. The formation of colloidosomes from the particle-covered bubbles does not appear to depend significantly on the charge of the particles, which makes it unlikely that bilayers of surfactant are stabilizing the colloidosome. While the exact mechanism of formation remains an open question, our method is a simple one-step process for obtaining colloidosomes from particle-covered bubbles.

1. Introduction

Fluid–fluid interfaces, which can trap and structure colloidal particles,^{1–3} are useful as templates for creating novel materials.^{4–7} For example, microporous capsules composed of colloidal particles suspended in water can be obtained by templating polyelectrolyte-modified particles onto octanol droplets, chemically binding the particles together, and subsequently dissolving the octanol phase.⁵ Such particulate capsules or ‘colloidosomes’, can also be made in water-in-oil systems by thermally sintering the adsorbed particles before transferring the particle-covered water droplets into an aqueous continuous phase.⁶ Further examples of colloidosomes include those composed of rod-shaped particles⁸ and those with gelled-aqueous cores.⁹ Note that the underlying principle of these synthetic routes is one of organizing particles on a well-defined interface in a system of immiscible phases and then removing the interface to obtain particle shells suspended in a single liquid phase. While much work has been done towards using emulsion droplets as templates for the formation of colloidosomes, we are unaware of any work that employs the gas–liquid interface as a template for producing these structures. Here we demonstrate that bubbles covered with polystyrene particles, so called ‘armored bubbles’, provide another route towards colloidosome-like structures.

During the course of our investigations on surfactant interactions with armored bubbles (e.g. ref. 10) we discovered that we could reproducibly obtain porous colloidal capsules when armored bubbles were exposed to the cationic double-chain

surfactant didecyltrimethylammonium bromide (DDAB). We observed that on exposure to the surfactant solution, the air phase of the bubbles dissolved while leaving behind the shells of close-packed particles as freely-suspended microporous capsules. These capsules, with a single aqueous phase both inside and outside, are similar to colloidosomes. This behavior is in contrast to that observed when bubbles are exposed to single-chain surfactants. Bubbles exposed to single-chain anionic^{10,11} or nonionic surfactants dissolve by ejecting single particles or particle aggregates from the interface.¹⁰

In light of this unexpected response of armored bubbles exposed to the cationic surfactant DDAB, we undertook a series of experiments focusing on double- and single-chain cationics, and pseudodouble-chain catanionic surfactants of various chain lengths at concentrations above their respective critical micelle concentrations (CMC) to more fully characterize our observations. While our main goal in this paper is to report our observations of the one-step formation of colloidosomes we also investigate the mechanism of the surfactant-mediated colloidosome formation, and find that the most obvious mechanism, an electrostatically-driven bilayer bridging at the scale of the particles, is not fully consistent with our observations. Preliminary experiments reveal the presence of a short-range attractive interaction between the particles on the bubble interface in the surfactant-free state, which may contribute to the formation of colloidosomes from armored bubbles.

2. Experimental

2.1 Preparation of armored bubbles

Armored bubbles were produced as in ref. 10. We employed 4.0 and 1.6 μm diameter anionic (sulfate charge groups) monodisperse spherical polystyrene latex particles and 1.5 μm diameter cationic (amidine charge groups) latex particles all purchased from Interfacial Dynamics Corp. All the

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particles used were certified surfactant-free by the manufacturer. 10 ml of an aqueous suspension of particles at a concentration of about 0.1 w/v% was shaken manually and vigorously for about 10 seconds in a 50 ml polypropylene centrifuge tube (Falcon). A dilute suspension of armored bubbles was obtained. The bubbles were allowed to sit in the tube for 10 minutes to allow sufficient time for dissolution to occur so that the majority of the bubbles achieved a stable nonspherical state.¹²

2.2 Surfactant experiments

Single-chain anionic surfactants, sodium octyl sulfate ($\geq 97\%$, $\text{CMC} = 2.9 \times 10^{-3} \text{ M}$)¹³ and sodium dodecyl sulfate ($\geq 98\%$, $\text{CMC} = 8.2 \times 10^{-3} \text{ M}$),¹⁴ were purchased from Sigma. Single-chain cationic quaternary ammonium surfactants $\text{CH}_3(\text{CH}_2)_{n-1}\text{N}(\text{CH}_3)_3(\text{Br})$, octyltrimethylammonium bromide ($n = 8$, $\geq 98\%$, $\text{CMC} = 1.4 \times 10^{-1} \text{ M}$),¹⁵ dodecyltrimethylammonium bromide ($n = 12$, $\approx 99\%$, $1.6 \times 10^{-2} \text{ M}$)¹⁵ and hexadecyltrimethylammonium bromide ($n = 16$, $\approx 99\%$, $\text{CMC} = 9.8 \times 10^{-4} \text{ M}$)¹⁶ were purchased from Sigma. The double-chain cationic quaternary ammonium surfactant $[\text{CH}_3(\text{CH}_2)_{n-1}]_2\text{N}(\text{CH}_3)_2(\text{Br})$, dioctyldimethylammonium bromide ($n = 8$, $\approx 97\%$, $\text{CMC} = 1.57 \times 10^{-2}$)¹⁷ was purchased from TCI America, and the double-chain cationic surfactants didecyltrimethylammonium bromide ($n = 10$, $\geq 97\%$, $\text{CMC} = 1.85 \times 10^{-3} \text{ M}$),¹⁸ didodecyltrimethylammonium bromide ($n = 12$, $\geq 98\%$, $\text{CMC} = 1.76 \times 10^{-4} \text{ M}$),¹⁸ ditetradecyldimethylammonium bromide ($n = 14$, $\geq 98\%$), dihexadecyldimethylammonium bromide ($n = 16$, $\geq 97\%$), and dioctadecyldimethylammonium bromide ($n = 18$, $\geq 98\%$), were purchased from Sigma. All surfactants were used as received.

The surfactant solutions were prepared with ultrapure water (Millipore) and allowed to equilibrate at room temperature for 24 hours before use. Each of the surfactant solutions was used at approximately twice the CMC except for the double-chain surfactants with chain lengths above 16. For these surfactants, solubility was poor and thus the solubility limit sets the concentration of the surfactant in solution. For the two double-chain surfactants with $n = 16$ and 18 we made suspensions at a concentration of 1 mg ml^{-1} , and note that substantial amounts of undissolved solid remained. We used the clear supernatant of these surfactant suspensions in our experiments.

We deposited 100 μl of the aqueous solution containing the armored bubbles onto a glass slide. Then, 500 μl of particle-free surfactant solution was deposited onto the aqueous drop containing the bubbles. Mixing due to interfacial stresses was rapid and rather violent due to the large difference in the surface tensions between the two solutions. The surfactant + bubble solution was left open to the atmosphere to promote the dissolution of the air phase,¹⁰ however, to minimize evaporation the slide was covered with the lid of a large Petri dish. The bubbles were observed with a Leica DM-IRB inverted microscope. Images of the bubbles were obtained with a high-resolution CCD camera (Retiga 2000R). The pH of the solution was measured with a pH indicator strip (colorpHast pH 0-14, EM-Reagents). The pH of the

solutions were ≈ 6.5 . All experiments were repeated at least three times.

2.3 Ostwald ripening experiments

To obtain a 'closed' chamber for the Ostwald ripening experiments, a 'Press-to-Seal' perfusion chamber (Molecular Probes) was adhered to a glass slide. The chamber had two access ports at either ends through which the bubble-containing solutions were introduced. We placed 100 μl of the bubble solution into the chamber. The access ports were sealed with an adhesive tab. Note that the seal was not air-tight. Bubbles were imaged with a CCD camera (Cohu). All experiments were carried out at room temperature.

3. Results and discussion

We performed new experiments with single-chain cationic quaternary ammonium surfactants but the results did not show any distinct differences from our earlier study.¹⁰ In a similar way to anionic and nonionic surfactants, armored bubbles exposed to these surfactants destabilized by continuously ejecting single particles and aggregates from the bubble interface as the air bubble dissolves. We refer the reader to our previous paper for details on bubble lifetime and response to single-chain surfactants.¹⁰

Our experiments with double-chain cationic quaternary ammonium surfactants, however, produced unexpected results. When an aqueous solution of didecyltrimethylammonium bromide (DDAB) was added to an aqueous suspension containing stable nonspherical bubbles covered with 4.0 μm diameter anionic charge-stabilized polystyrene latex particles (Fig. 1a), the initially nonspherical bubbles return to a spherical shape, with many of the smaller bubbles showing striking changes in optical contrast (compare Fig. 1a and b). Indeed, observations of larger 'bubbles' in the suspension reveal that a spherical region of dark contrast shrinks and vanishes within a spherical shell of colloidal particles (Fig. 1b–d).

Based on these observations, we conclude that the air bubble enclosed by the particle shell dissolves on exposure to the surfactant solution. As the air bubble dissolves, there is dewetting of the contact line, and the bulk aqueous solution infiltrates through the interstitial pores of the close-packed shell of particles. The shell of particles are thus the walls of an intact capsule of colloidal particles suspended in the surfactant solution. We emphasize that these capsules now do not enclose a gas phase, but rather have the *same aqueous phase in their interior as their exterior*, and consequently are similar to colloidosomes.^{5,6} We have made many observations of the disappearance of the gas phase and formation of colloidal capsules upon exposure of DDAB to initially stable armored bubbles (Fig. 1e and f).

Along with intact spherical capsules, we also observe freely-floating curved monolayers of colloidal particles in solution which appear to be sections of a spherical shell (Fig. 2). We note that the colloidal capsules are rather fragile and do not survive strong fluid shear forces; thus these curved monolayers appear to be fragments of capsules that broke due to strong fluid shear forces during the initial mixing of the surfactant and bubble solutions (see the Experimental section). Although

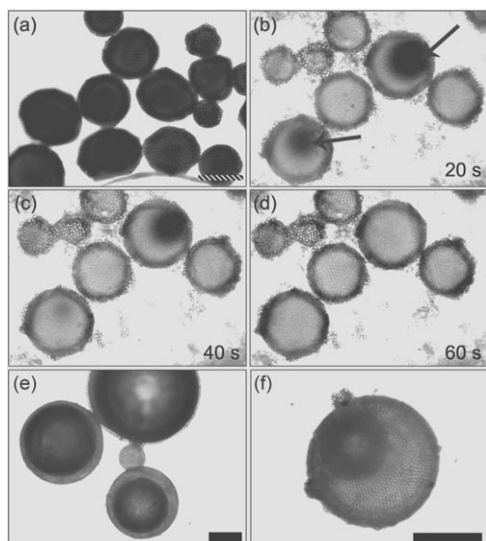


Fig. 1 Bright-field optical micrograph of armored ‘bubbles’ covered with anionic polystyrene particles being exposed to didecyldimethylammonium bromide at $2\times$ its CMC. pH of the solution was ≈ 6.5 . (a) Stable nonspherical armored bubbles prior to exposure to the surfactant solution. Particles are $4.0\ \mu\text{m}$ in diameter. Images have been overexposed so that the armored bubbles that enclose a gas phase appear dark against a bright background. (b) 20 seconds after exposure, a snapshot of the sample reveals that most of the armored ‘bubbles’ have returned to a spherical shape with a significant change in contrast evident. Some of the ‘bubbles’ still have a dark spherical object inside them (black arrows). (c) The region of dark contrast progressively disappears, shown here as a snapshot at 40 seconds. (d) At 60 seconds only spherical particle shells remain in solution, all of them with light contrast against the bright background. (e, f) Intermediate stages of colloidosome formation with bubbles covered with $1.6\ \mu\text{m}$ diameter polystyrene particles. The dissolving air bubble can be seen more clearly through the thinner shell of particles. Scale bars $40\ \mu\text{m}$.

we observe both intact capsules and capsule fragments, to simplify the following discussion, we will refer to these structures collectively as colloidosomes.

To further characterize the observation, we systematically varied the surfactant structure, *i.e.* the number of hydrophobic chains and the hydrophobic chain length. Polydisperse samples of armored bubbles covered with $1.6\ \mu\text{m}$ diameter anionic polystyrene particles were each exposed to cationic quaternary ammonium surfactants of chain length $n = 8\text{--}18$, respectively. The bubble and surfactant solutions were left for 15 minutes to allow time for the dissolution of the air phase. After 15 minutes, the presence of aggregates or colloidosomes was determined by manual observation of the particle + surfactant suspension using an optical microscope. The results of the experiments are summarized in Table 1.

For double-chain surfactants with shorter chain lengths $n = 8, 10, 12$ and 14 we obtain colloidosomes. For the longer chain lengths $n = 16$ and 18 we find that the air phase of the armored bubbles was still stable after the 15 minute incubation time. We continued observing these samples for an hour and found that the bubbles remain nonspherical and stable. After three hours we found that the air phase of the smallest bubbles does dissolve, however instead of leaving behind well-struc-

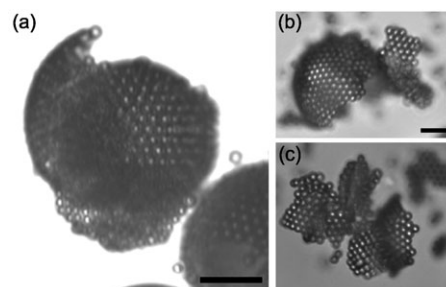


Fig. 2 Images of colloidal monolayer fragments seen in solution after armored bubbles covered with $4.0\ \mu\text{m}$ polystyrene particles are exposed to didecyldimethylammonium bromide at $2\times$ its CMC. pH of the solution was ≈ 6.5 . (a) Image of two air bubbles with broken sections of colloidosomes still adhering. (b, c) Colloidal fragments that are found in solution. Most of the fragments are curved which is a reflection of the curvature of the templating bubble. Scale bars $24\ \mu\text{m}$.

tured spherical shells, aggregates of particles were obtained. Surface tension measurements in solutions of dioctadecyldimethylammonium bromide ($n = 18$) vesicles show that this surfactant is only weakly surface active due to its low solubility in water.¹⁹ Indeed, our observation that the bubble remains nonspherical and stable for several hours is similar to our previous observations of armored bubbles exposed to extremely low concentrations of water-soluble surfactants.¹⁰ Single-chain surfactants of all chain lengths tested gave either single particles or small unstructured particle aggregates.

To increase the number of double-chain surfactant types for our experiments, we employ a well-known property of charged single-chain surfactants: in aqueous solutions surfactant molecules of opposite charge can pair up to form pseudodouble-chain catanionic surfactants.²⁰ Intriguingly these pseudodouble-chain surfactants are known to form equilibrium unilamellar vesicles in solution.²⁰ We formed a broad range of symmetric and non-symmetric pseudodouble-chain surfactants by adding equimolar concentrations of anionic and cationic single-chain surfactants. Note that we did not carefully characterize the CMC of each catanionic surfactant solution. We determined that the concentration of the surfactant solutions were above the CMC by two means: (i) The solutions of single-chain surfactants used were all above their CMC, and pseudodouble-chain surfactants have CMCs that are lower than that of the parent surfactants. (ii) We visually confirmed the presence of vesicles, lamellar phases or insoluble precipitate in these surfactant mixtures. We expose the armored bubbles to these pseudodouble-chain surfactants and find that we once again obtain colloidosomes in every case, *i.e.*, for all combinations of chain lengths tried. The results of our experiments with various cation–anion surfactant pairs are summarized in Table 1.

We next consider the question of why do armored bubbles that are exposed to double-chain and pseudodouble-chain surfactants produce colloidosomes? To recap, in our experiments the armored bubbles start out being nonspherical and stable to dissolution¹² in surfactant-free water (Fig. 3a). When cationic single-chain or double-chain surfactants are added to the solution, the bubbles return to a spherical shape before the air phase starts to dissolve (Fig. 3b). It is apparent that the particle–fluid interface interactions are being modified when

Table 1 Structures obtained when bubbles covered with 1.6 μm diameter anionic fluorescent polystyrene particles (sulfate charge groups) are exposed to (upper two rows) cationic quaternary ammonium surfactant solutions at concentrations $\approx 2 \times \text{CMC}$ and (lower row) a mixed solution of single-chain cationic and anionic surfactants (a catanionic system) at concentrations above the CMC. pH of the solution was ≈ 6.5

Number of chains	Hydrophobic chain length					
	8	10	12	14	16	18
1	Aggregates ^a	^b	Aggregates	^b	Aggregates	^b
2	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes	No change ^c	No change
Number of chains	8 : 8 ^d	8 : 12	8 : 16	12 : 8	12 : 12	12 : 16
2	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes

^a Particles were released from the bubbles as singlets and/or as aggregates. ^b Experiments not done with this surfactant type. ^c Air phase still stable after 1 hour of exposure to surfactant solution. ^d Catanionic system (anion chain length : cation chain length).

the surfactants are introduced into the system, for the contact angle on the particle must change from about 40° ²¹ to 0° as the bulk aqueous phase infiltrates through the particle shell. It has been proposed that surfactants render the particles more hydrophilic by adsorbing onto the particle surface with the hydrophilic head predominantly away from the hydrophobic particle surface.^{10,11} Consequently, the adsorption of surfactant favors the displacement of the particles into the water phase, with the surfactant molecules replacing the particles at the gas–liquid interface. Once the surfactant molecules have displaced the particles from the bubble interface, the gas bubble, which is now being stabilized by only water-soluble surfactants, will continue to dissolve due to its Laplace overpressure.¹⁰ Thus it seems rational that both double-chain and single-chain surfactants cause the dissolution of the air phase.

The second effect to consider is particle–particle interactions, *i.e.* attractive or repulsive interactions between the particles on the bubble interface. In the case of single-chain surfactants, as the bubble dissolves, particles are continuously released as Brownian singlets or small aggregates into solution¹⁰ (Fig. 3c), which suggests that the neighboring particles do not experience significant attractive interactions. In contrast, for the case of bubbles exposed to double-chain surfactants, the particles remain locked in a shell-like structure, with the gas bubble dissolving within the shell (Fig. 3c), which would require the particles to occupy an attractive minimum that is at least greater than $k_B T$. What could be the cause of this attractive minimum? An important distinguishing chemical feature between double- and single-chain surfactants is that double-chain (and pseudodouble-chain) surfactants form bilayers and lamellar phases in solution.²² Furthermore, it has been proposed that planar colloidal crystals (composed of anionic polystyrene particles) which grow on the surface of vesicles composed of a mixture of Triton X-100 and the cationic double-chain surfactant didodecyltrimethylammonium bromide are held together by an electrostatically adsorbed bilayer of surfactant.²³ There are also reports of bilayer deposition from unilamellar vesicles of dioctadecyltrimethylammonium bromide on anionic polystyrene particles.²⁴ Thus *a priori* it seems rational to hypothesize that double-chain surfactants stabilize the colloidosome by forming a bilayer between adjacent particles, thus binding the particles together. However, this mechanism is deemed less likely as a result of additional experiments, which we describe below.

Formation of an adsorbed bilayer can be pictured as follows: charged surfactant molecules adsorb onto oppositely charged sites on the particles by first forming a monolayer with the chain oriented away from the particle surface. Additional surfactant molecules then adsorb onto the chains of the previously adsorbed monolayer, due to hydrophobic attraction between the surfactant chains, with their hydrophilic headgroups oriented away from the particle surface, thus forming a bilayer.^{25–27} However, when both the surfactant headgroup and the surface have the same charge, adsorption at the charge sites should not occur. Thus bilayers are not expected to form when both the surfactant and the particle have the same charge. Indeed, experiments with suspensions of

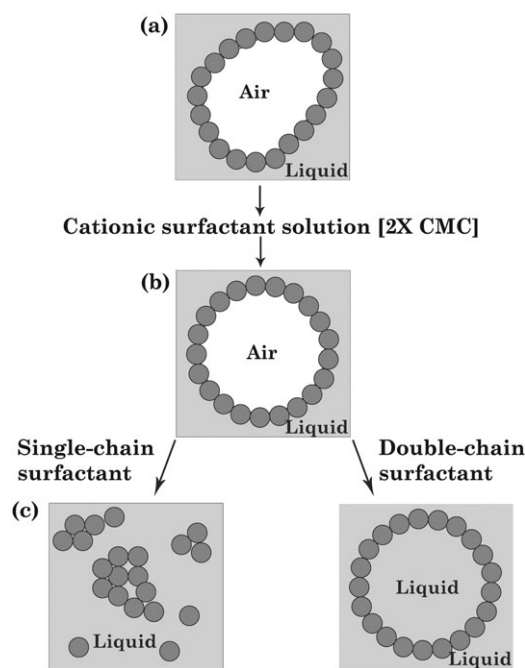


Fig. 3 Schematic of experimental observations when armored bubbles are exposed to cationic surfactant solutions. (a) Armored bubbles that are stable to dissolution are nonspherical in air-saturated water.¹⁰ (b) Bubbles are exposed to a cationic surfactant solution at a concentration $2 \times \text{CMC}$. The nonspherical bubbles return to a spherical shape and the gas phase proceeds to dissolve. (c) The structures that are obtained after dissolution of the gas phase are particle aggregates and singlets for single-chain surfactants or colloidosomes for double-chain surfactants.

Table 2 Structures obtained when bubbles covered with 1.5 μm diameter cationic polystyrene particles (amidine charge groups) are exposed to (upper two rows) cationic quaternary ammonium surfactant solutions at concentrations $\approx 2 \times \text{CMC}$, and (lower row) a mixed solution of single-chain cationic and anionic surfactants (a catanionic system) at concentrations above the CMC. pH of the solution was ≈ 6.5

Number of chains	Hydrophobic chain length					
	8	10	12	14	16	18
1	Aggregates ^a	^b	Aggregates	^b	Aggregates	^b
2	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes	No change ^c	No change
Number of chains	8 : 8 ^d	8 : 12	8 : 16	12 : 8	12 : 12	12 : 16
2	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes	Colloidosomes

^a Particles were released from the bubbles as singlets and/or as aggregates. ^b Experiments not done with this surfactant type. ^c Air phase still stable after 1 hour of exposure to surfactant solution. ^d Catanionic system (anion chain length : cation chain length).

small bilayer vesicles of the anionic surfactant asolecithin and anionic polystyrene particles have shown the adsorption of only a monolayer of surfactant on the particles.²⁸ It follows that the hypothesis of bilayer stabilization of the colloidosome is testable: we repeat the above experiments keeping the charge of the surfactant the same (*i.e.* cationic) but this time using cationic amidine particles.²⁹ We observe the formation of colloidosomes (see the ESI†) for all cases as seen previously, however, relatively more fragments and broken colloidosomes are formed, which indicates the weaker interparticle adhesion in this case. The results of our experiments are summarized in Table 2. The catanionic surfactants also produced colloidosomes (Table 2). Since we observe colloidosome formation when both the particles and the surfactant have the same charge, it does not appear to us that bilayer formation is the defining feature for explaining how double-chain surfactants provide interparticle adhesion that supports colloidosome formation.

As a first step towards elucidating the complete mechanism of colloidosome formation we qualitatively probed the particle–particle interactions on the armored bubbles in the absence of surfactants. We placed a polydisperse sample of

armored bubbles into a closed chamber along with a few uncovered bubbles. Bubbles in this ‘closed’ system will undergo Ostwald ripening, which is the diffusion of gas from bubbles with higher pressure (bubbles with smaller radii) to bubbles with lower pressure (bubbles with larger radii).²⁶ Consequently, larger bubbles will grow at the expense of smaller bubbles. Since the particles all have the same charge, the naïve expectation is that an initially-stable nonspherical armored bubble which grows will evolve with all the particles dispersing uniformly over the expanding surface of the bubble to minimize their repulsive interactions. Thus, by observing particle dynamics on a growing bubble, we can infer the interactions between the particles on the bubble surface at the close-packed state. Note that large interparticle spacing and crystalline ordering of the particles have been observed for particles adsorbed on planar fluid–fluid interfaces,³⁰ and emulsion droplets²³ and also in the case of armored bubbles produced with only sparse surface coverage of particles (before the bubble dissolves and the particles come into contact).¹² However, we observe that in a surfactant-free solution a growing armored bubble cracks its particle shell as gas enters the growing bubble (Fig. 4). Cracking of the particle shell indicates that the particles are trapped in an attractive minimum (van der Waals forces may be operational) prior to the addition of any surfactants, and that the shell fails along a weakness as it is strained by the expanding gas bubble.

Looking forward, we believe it is important to consider the effect surfactants have on the capillary forces that operate on the particles as the gas–liquid interface recedes. Another effect to consider is the role surfactants play in modifying interactions present between the particles on the surface of the armored bubble. For example, is it possible that single-chain surfactants with their smaller molecular diameter might fit in between particle–particle contacts and promote redispersion of the particles, while double-chain surfactants do not? Finally, it would be interesting to determine if our observations of colloidosome formation extends more generally to other particle types.

4. Conclusion

We have shown that bubbles covered with cationic and anionic polystyrene latex particles exposed to double-chain quaternary ammonium surfactants and catanionic surfactants at concentrations above the surfactant CMC form colloidosomes: there

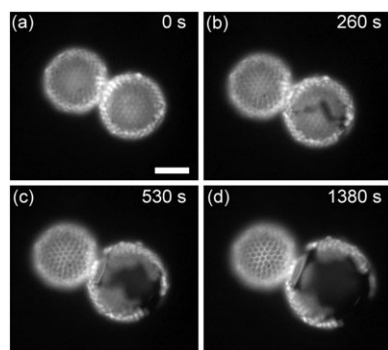


Fig. 4 A pair of bubbles undergoing Ostwald ripening in a closed chamber. The system is free of surfactants. Both bubbles are covered with 4.6 μm diameter fluorescent anionic polystyrene particles. (a) The bubbles both have a close-packed layer of particles on their surface. (b) Due to gas diffusion between bubbles in the bulk (*i.e.* not in this picture), the lower bubble starts growing and a crack appears on its surface after 260 seconds. (c, d) The crack becomes progressively larger and there is no redispersion of the particles on the bubble surface. The bare air–water interface reflects the light emitted by the particles on the neighboring bubble. Scale bar 28 μm .

is a particle shell with the same aqueous phase inside and out. Our observations with a specific subset of quaternary ammonium surfactants and cationic surfactants suggests that the formation of colloidosomes from armored bubbles cannot be fully explained by the formation of bilayer bridges between the particles. Qualitative probing of the interactions between the colloidal particles in the absence of surfactant reveals an adhesive force between the particles, which is most likely due to van der Waals interactions. Such dispersion forces that act to stabilize the colloidosomes are expected to be relatively weak, which may also rationalize why these capsules are rather fragile and do not survive strong fluid shear forces. We conclude by emphasizing that the surfactant-mediated formation of colloidosomes that we have demonstrated provides a simple one-step method for forming microstructured porous capsules from armored bubbles.

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