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The hydrophobic modification of kappa carrageenan microgel particles for the stabilisation of foams

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Abstract

Hypothesis

Polysaccharides such as kappa carrageenan are often utilised in fat replacement techniques in the food industry. However, the structural role they can provide within a product is limited by their hydrophilic nature. Hydrophilic particles can be surface-activated by hydrophobic modification e.g. *in-situ* interaction with a surfactant. This can drastically improve foam stability by providing a structural barrier around bubble interfaces offering protection against disproportionation and coalescence. Hence, it should be possible to bind negatively charged kappa carrageenan particles with a cationic surfactant through electrostatic interaction, in order to alter their surface properties.

Experiments

Lauric arginate was mixed with kappa carrageenan microgel particles at various concentrations and the potential electrostatic interaction was studied using zeta potential, turbidity and rheological measurements. Mixtures were then aerated and foaming properties explored, in particular the location of the particles.

Findings

Lauric arginate was successfully bound to kappa carrageenan microgel particles. Consequently, particles were surface-activated and adsorbed at the air/water interface, as shown by optical and confocal microscopy. Foam half-life peaked at an intermediate surfactant concentration, where there was sufficient surfactant to coat particle surfaces but the concentration was low enough to prevent the formation of large aggregates unable to adsorb at the a/w interfaces.

Keywords

Microgel

Fluid gel

Particles

Biopolymer

Surface-activation

Foam

Pickering stabilization

1 Introduction

Aqueous foams are thermodynamically unstable systems, which collapse via liquid drainage, disproportionation and coalescence. Surfactants provide limited stability against these mechanisms by lowering the surface tension [1]. Foam stability can be dramatically improved via the adsorption of particles to the air/water (a/w) interface, termed Pickering stabilisation [2], which provides a structural barrier to coalescence and disproportionation [3]. Particles need to have intermediate hydrophobicity and be partially wetted in order to adsorb at an interface. Hydrophilic particles therefore need to be modified, typically either by chemical modification or *in situ* modification with surfactants. There are many examples of particle-surfactant combinations used to stabilise foams in the literature, a few of which are: laponite clay particles with hexylamine [4], alkylammonium bromides [5] or CTAB [6], alumina particles with short chain carboxylic acids [7] and calcium carbonate particles with SDS [8]. However, none of these combinations are suitable for food-grade systems. There are several reviews on food-grade particles for Pickering stabilisation but these mainly focus on emulsion systems [9-11] and those that do investigate foams [12, 13] have generally not studied particle-surfactant combinations. Recently however, Binks, Muijlwijk [14] have studied the modification of calcium carbonate particles with various anionic surfactants for potential use in food systems. The modification of hydrophilic particles using surfactants *in-situ* is therefore an exciting emerging area of research for the food industry, which is only just starting to be utilised.

One of the major challenges facing the food industry is the increasing Government and consumer pressure to reduce the levels of fat in food products. Diets high in fat, especially the saturated kind, can lead to high cholesterol and increase the risk of heart disease [15].

63 Polysaccharides are commonly used in fat replacement techniques. As well as their low cost
64 and high abundancy, they have the ability to structure water [16-18] and mimic the
65 structural characteristics of oil droplets when in particulate form [19]. This has been enabled
66 by the development of fluid gels; suspensions of gelled particles dispersed in a non-gelled
67 continuous phase [20]. In addition, as many polysaccharides can be classified as vegan, their
68 use in reduced fat systems is of strong interest to the food industry as the demand for vegan
69 products escalates [21].
70
71 However, the hydrophilic nature of polysaccharides limits their use in food product
72 microstructure design. Hydrophobic modification and subsequent potential surface
73 activation of polysaccharide particles would therefore significantly increase their
74 functionality in such products, for example by enabling them to adopt a more important
75 structural role (similar to that of fat droplets in whipped cream [22]). The majority of
76 polysaccharides used in the food industry are anionic e.g. carrageenan, alginate, pectin and
77 xanthan. A cationic surfactant would therefore be required for potential electrostatic
78 interaction and subsequent surface-activation. Lauric arginate (LA) is one such surfactant,
79 which has been approved as generally regarded as safe (GRAS) within the United States for
80 certain food applications [23]. There are a small number of studies in the literature that
81 focus on the interaction between LA and anionic biopolymers; Bonnaud, Weiss [24] describe
82 a strong binding interaction between LA and anionic biopolymers pectin, alginate,
83 carrageenan and xanthan, indicated by isothermal titration calorimetry. Asker, Weiss [25]
84 suggest that the addition of pectin to mixed LA/Tween 20 micelles leads to the formation of
85 electrostatic complexes that have potential applications as functional ingredients. However,
86 to the best of the authors' knowledge, this is the first study that investigates the potential

surface-activation of polysaccharide particles through binding of LA for use in aqueous foams.

Kappa carrageenan (κC) was selected as the polysaccharide to study and was prepared in fluid gel form in order to create microgel particles. It was chosen because firstly, it is strongly negatively charged and so has a high potential for electrostatic interaction with LA and secondly, microgels have shown interesting interfacial behaviour, primarily the ability to deform upon adsorption to an interface. Microgels are an increasingly interesting area of research due to their vast potential as colloidal building blocks and stabilising agents due to their deformability, surface activity, reversible swelling behaviour and responsiveness to pH and temperature [26]. A number of studies have demonstrated the ability of microgels to adsorb to a fluid or a/w interface by diffusion-limited adsorption and subsequently deform in order to maximise exposure [27-30]. Furthermore, Dickinson [26] recently highlighted the significant, novel potential of biopolymer-based microgels to stabilise food emulsions and foams.

2 Materials and methods

2.1 Materials

Kappa carrageenan (22048) and Tween 20 (≤3.0% impurities) were purchased from Sigma Aldrich (UK). Lauric Arginate was obtained in the form of Cytoguard LA 2X (A&B Ingredients, USA) in a liquid form with propylene glycol carrier and a 20% content of Lauric Arginate. All were used without further purification and concentrations were calculated as weight percentage.

2.2 Preparation of fluid gel

Kappa carrageenan (1 wt%) was dispersed in deionised water at room temperature, then heated to 70 °C. The solution was transferred into a cooled jacketed pin stirrer through a peristaltic pump at 70 °C. The outlet temperature was controlled to 5 °C to ensure gelation occurred under shear (gelation temperature ≈ 25 °C). A retention time of 7.5 min was achieved through using a pump speed of 20 $mLmin^{-1}$, resulting in a cooling rate of 8 $°Cmin^{-1}$. The shaft rotation speed was set to 1500 rpm to give a narrow distribution of particle size [31]. Fluid gels were stored at 5 °C.

2.3 Preparation of κC fluid gel-LA complexes

1% κC fluid gel was diluted 1:1 with deionised water. LA at various concentrations was then added to the solution whilst stirring for 5 days at room temperature.

2.4 Zeta potential measurements

Zeta potential was determined using a Zetasizer (Malvern Instruments, UK) at 25 °C. κC fluid gel was diluted and its pH was altered from 1.5 to 10 using either NaOH or HCl of 1M concentrations. Complexes were measured at their natural pH. All data points were carried out in three replicates.

2.5 Turbidity measurements

The turbidity of κC fluid gel-LA complexes was inferred from the absorbance at 600 nm using a UV-Vis spectrophotometer (Orion AquaMate, Thermoscientific, UK) in 1 cm cuvettes against deionised water. Measurements were carried out at 25 °C in three replicates.

2.6 Rheology

A Kinexus rheometer (Malvern Instruments, UK) was used to perform rheological measurements at 25 °C. κC fluid gel-LA complexes were tested after 24 h to ensure post-production particle ordering completion [32, 33]. All measurements were conducted using a serrated parallel plate of 60 mm diameter set to a 1 mm gap. Amplitude sweeps were conducted at a frequency of 1 Hz as a function of applied oscillatory strain. All experiments were carried out in three replicates.

2.7 Surface tension

Surface tension measurements of κC fluid gel-LA complexes and LA solutions were performed using a Kruss GmbH K100 tensiometer (Hamburg, Germany). The Wihelmy plate method was used to measure static surface tension at an immersion depth of 2mm at 25 °C. Experiments were carried out in three replicates. The critical micelle concentration (CMC) was calculated as the concentration at which surface tension stopped decreasing (Figure 6), which was 0.15 wt% for LA solutions. This was similar to values reported in the literature: 0.18-0.21 wt% [24, 34]. The slight difference may have been a result of a difference in the source of Lauric Arginate or in the method of obtaining CMC as isothermal titration calorimetry was used in the referenced literature.

2.8 Aeration

κC fluid gel-LA complexes of equal volumes were aerated using a Hobart mixing unit. The highest speed setting was used for 7 min as this ensured air fraction was high for all systems

(between 0.65-0.95: the wet foam boundary). Air fraction was determined to assess foam ability using Equation 1, by weighting equivalent volumes of fluid gel and foam, using three replicates.

$$\text{Air fraction} = 1 - \left(\frac{m_{\text{foam}}}{m_{\text{fluid gel}}}\right) \quad \text{Equation (1)}$$

Overall foam stability was measured using half-life measurements, that is the time taken to reduce the height of the foam by half. The reduction of the foam height was recorded using a CCD camera and the half-life was later calculated for three replicates (three separate batches).

2.9 Liquid drainage and foam structure measurements

Liquid drainage and bubble size measurements were conducted using a Krüss DFA100LCM foam analyser (Krüss, Germany). The κC fluid gel-LA mixture was poured into the foam cell to cover the reference electrode followed by the externally produced foam. The decrease in liquid fraction was then recorded using electrical conductivity measurements at 7 pairs of electrodes along the cell height. Drainage profiles were recorded at sensor 3 (positioned at half the foam height) for the first four hours from initial aeration. Bubble sizes were recorded using a high resolution camera at a similar foam height. Experiments were carried out in three replicates (three separate batches).

2.10 Optical microscopy

Aerated κC fluid gel-LA complexes were imaged using phase contrast microscopy (Leica Microsystems, UK). The sample was placed onto a microscope slide with a coverslip and observed using objective lenses up to 40x magnification.

2.11 Confocal microscopy

The microstructure of aerated κC fluid gel-LA complexes as well as κC fluid gel particles before complexation (1 wt% κC) were visualised using a confocal scanning laser microscope (Leica TCS SPE, Heidelberg, Germany). The κC fluid gel-LA complexes were aerated, placed onto a microscope slide and stained with 0.01 wt% rhodamine B (Sigma Aldrich, Dorset UK). A coverslip was then placed over the sample and a laser operating at a wavelength of 532 nm was used for imaging.

3 Results and Discussion

3.1 Production and characterisation of kappa carrageenan fluid gel

The gelling mechanism of kappa carrageenan (κC) is widely accepted as a thermally-reversible coil-to-helix transition followed by helix aggregation in the presence of K^+ ions [35]. During fluid gel preparation, this process occurs under shear resulting in the production of gel particles dispersed in a continuous phase, typically water [20]. The κC particles behave as soft microgel particles with penetrable "hairy" chains allowing for particle overlap and interaction [36]. A fluid gel was produced at 1 wt% by shearing a hot solution of κC whilst it underwent gelation in a cooled jacketed pin stirrer at a shaft rotation speed of 1500 rpm. Garrec, Guthrie [36] previously estimated the κC fluid gel particle volume fraction at 1 wt% as 0.65, here the fluid gel was diluted by half in order to study a less concentrated suspension. Unfortunately, the particles cannot be visualised using optical microscopy as the refractive index of κC is too close to that of the water continuous phase (1.334). However, particles could be imaged using confocal microscopy (Figure 1a), particle diameter appeared to be in the 10-50 μm range.

The zeta (ζ) potential of a diluted 1% kappa carrageenan (κC) fluid gel was measured over a pH range. At natural pH (6.8), ζ-potential was -53.1 ± 2.9 mV (Figure 1b), indicating κC particles were strongly negatively charged. This can be attributed to their ester sulphate groups. ζ-potential remained constant over a wide pH range, only changing considerably at pH 1.5 where particles became less negatively charged due to protonation of κC under strong acidic conditions (Figure 1b). The ζ-potential of Lauric arginate (LA) at natural pH (2.3) was +23.8 ± 3.9 mV, which confirmed its positive charge (Figure 1b). The potential

electrostatic interaction between κC and LA was therefore investigated at their natural pH and as a function of LA concentration.

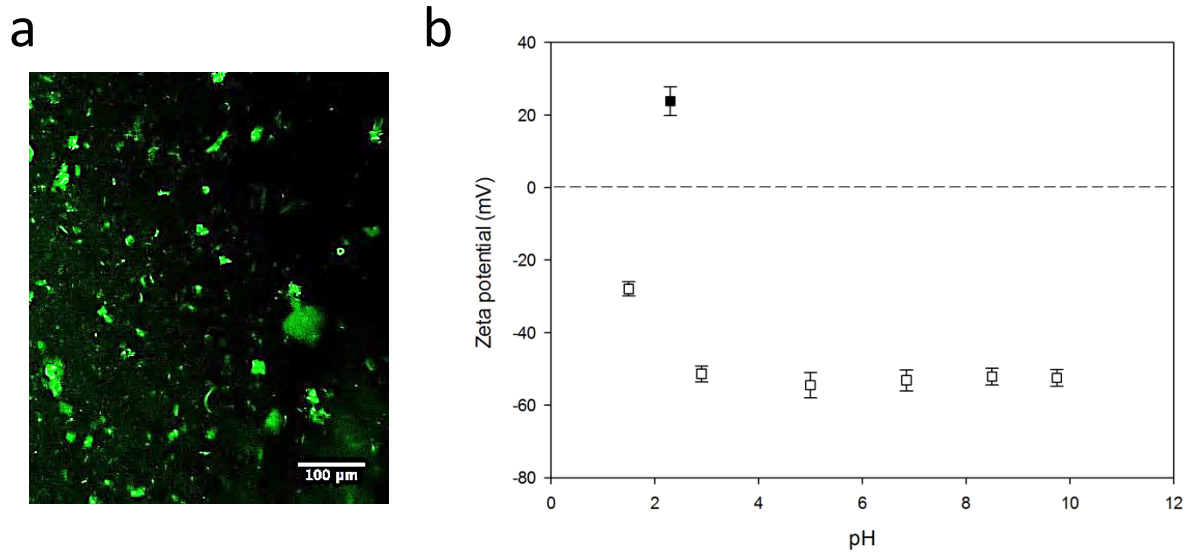


Figure 1: (a) Confocal micrograph of diluted 1 wt% κC fluid gel particles at natural pH (6.8) dyed with rhodamine B. (b) Zeta potential measurements of diluted 1 wt% κC fluid gel (□) over a pH range and of LA at natural pH (■).

3.2 Complex formation through surfactant binding

LA was added at various concentrations to a diluted 1% κC fluid gel solution. Zeta potential, turbidity and rheological measurements were used to analyse the interaction. The ζ-potential of κC particles were measured 24 h after production. At 0% LA, ζ-potential was -53.1 ± 2.9 mV, reflecting its negatively charged ester sulphate groups. Upon increasing LA concentration, ζ-potential became increasing less negative until it reached zero at 0.15% LA (Figure 2). This suggests that monomers of LA were binding to κC particles reducing their negative charge and at 0.15% LA, sufficient surfactant had been added to neutralise the charge. The electrostatic interaction was facilitated by the cationic head group (L-arginine) of LA and the negatively charged sulphate groups of κC particles. It has often been reported in the literature that the ζ-potential of negatively charged particles mixed with cationic surfactants continued to increase with surfactant concentration after this charge neutralisation had occurred [5, 8, 37]. This was a result of a second layer of surfactant

adsorbing onto the initial monolayer through hydrophobic interactions. However, increasing the concentration of LA beyond 0.15% (to 0.2%) revealed a decrease in ζ-potential to -3.8 ± 1.8 mV. A return to a negative ζ-potential suggests that a bilayer of surfactant cannot form and instead added surfactant is most likely residing in the continuous phase.

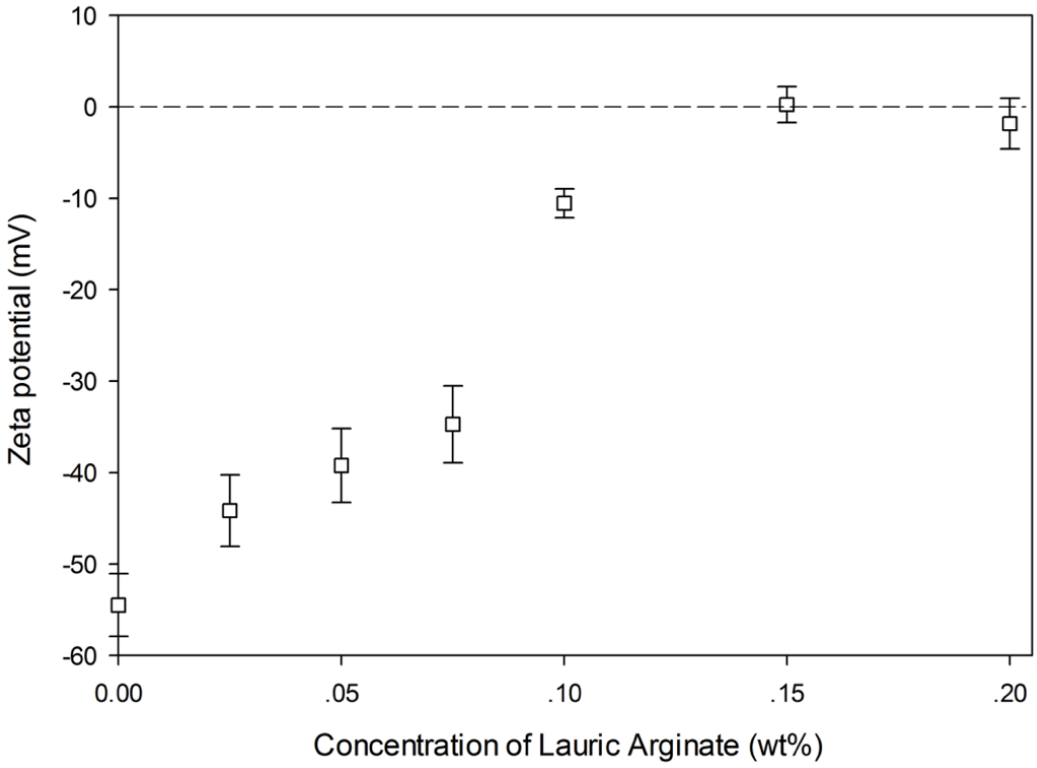


Figure 2: Zeta potential measurements of κC fluid gel particles as a function of increasing LA concentration. Concentration is calculated as wt% of the total solution.

Visible observations of κC fluid gel + LA solutions confirmed a change in their structure with increasing LA concentration (Figure 3a). Solutions increased in turbidity but remained homogenous in appearance until 0.1% LA. From 0.1% LA increasingly large aggregates were observed using optical microscopy, ranging from 100 μm to 300 μm in size. Turbidity was measured using a UV-Vis spectrophotometer to quantify these observations. Absorbance can be seen to increase linearly with LA concentration (Figure 3b). At 0.15% and 0.2% LA, the error bars in absorbance data were considerably larger, due to substantial aggregates observed in the solutions. This turbidity data provides further evidence of complex

formation, where an increase in turbidity (scattering of light by particles) corresponds to an increase in particle density, due to electrostatically bound surfactant. It is also clear that aggregation of the complexes occurred, especially at higher LA concentrations. This was caused by a reduction in particle charge, which led to less repulsion and therefore more intermolecular interactions between particles. This effect was heightened at 0.15% LA and 0.2% LA as charge neutralisation of the complexes considerably limited their solubility. A similar trend was first observed by Bonnaud, Weiss [24] where turbidity initially increased at low concentrations of LA when mixed with iota-carrageenan, indicating the formation of complexes. Larger aggregates were then observed at concentrations of 0.03-0.23 wt% LA.

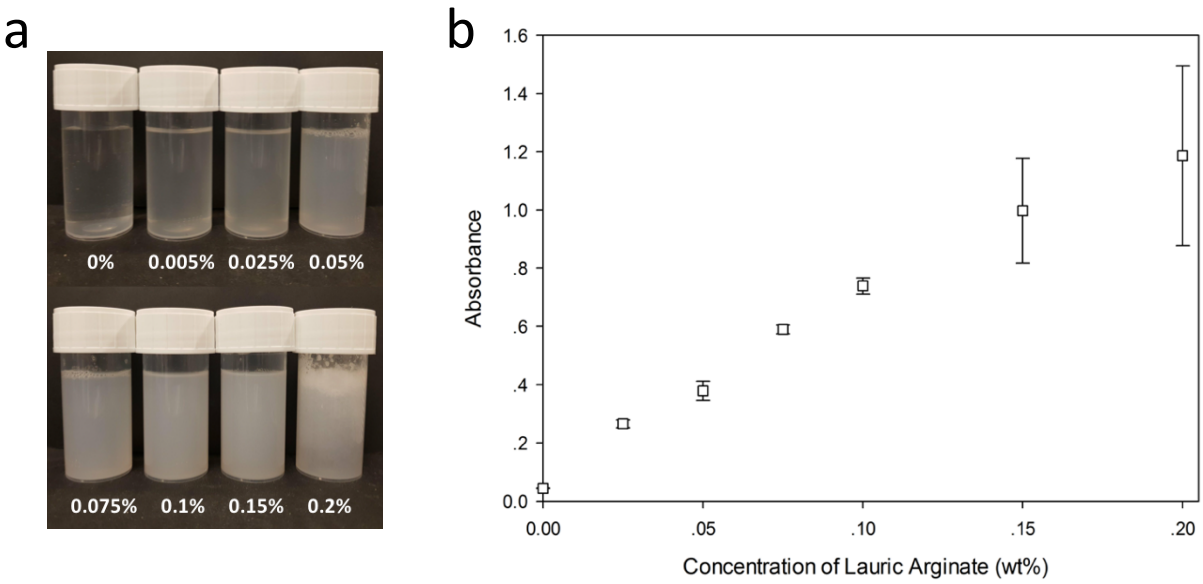
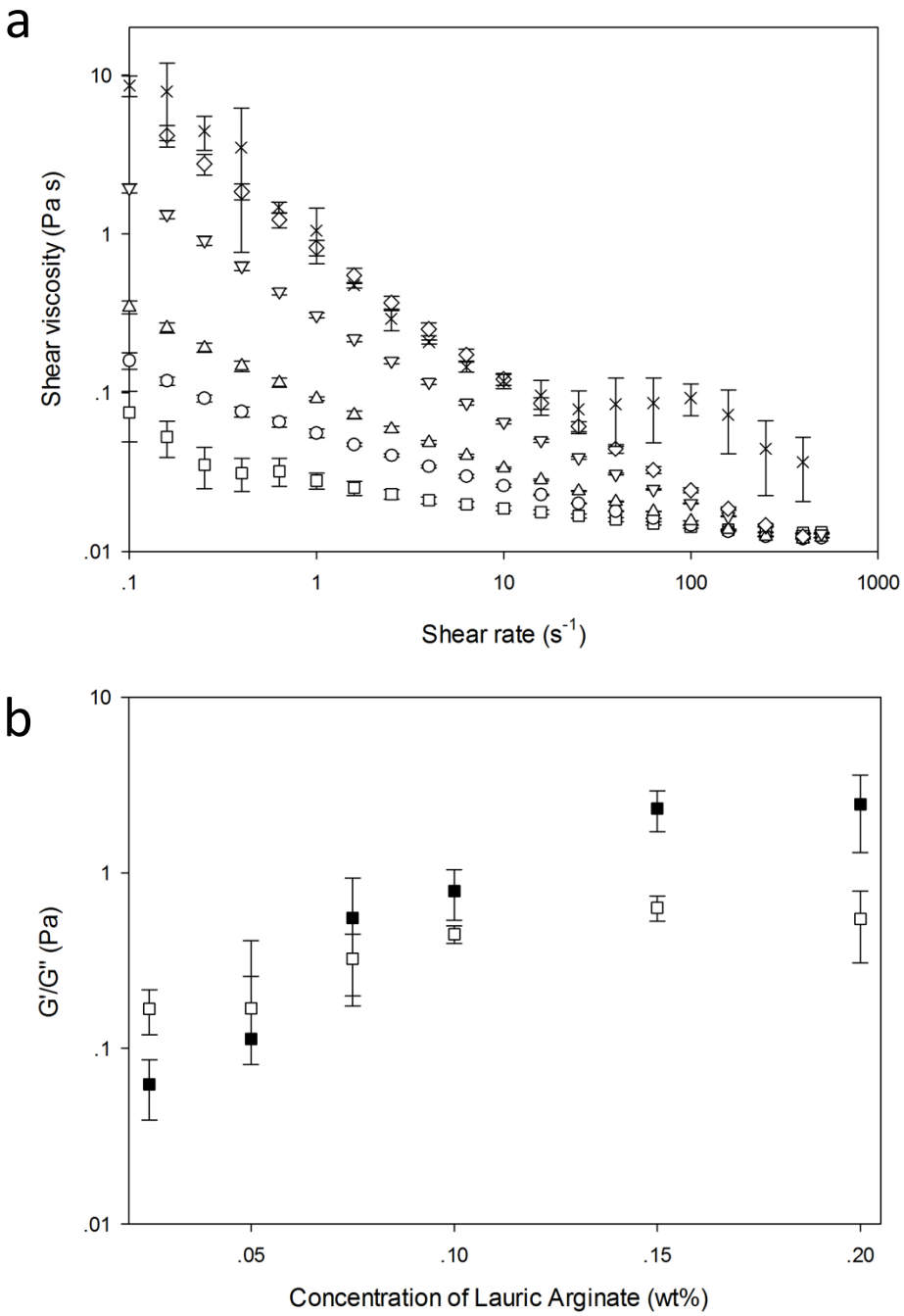


Figure 3: (a) Photographs of solutions of κC fluid gel particles mixed with LA at various concentrations. (b) Absorbance of the same solutions, measured using a UV-Vis spectrophotometer.

The bulk viscosity of foams affect the mobility of the continuous phase and therefore drainage velocity [38]. It is therefore essential to understand the rheological responses of these fluid gels to understand how they behave when aerated. The viscosity profiles of κC fluid gel complexes at various LA concentrations were measured (Figure 4a). The flow curves at all LA concentrations exhibited strongly shear thinning behaviour. This is typical of fluid

279 gels at low volume fractions, where they behave as highly aggregated suspensions
280 dominated mainly by colloidal forces [39]. At higher volume fractions, particles behave as
281 soft microgels where rheology is dependent on particle elastic modulus as well as particle-
282 particle interactions [32, 40]. From Figure 4a, at low shear rates a difference in fluid gel
283 viscosity can be observed, where it increased with LA concentration. However at high shear
284 rates, most fluid gels displayed a similar viscosity. This further confirms the difference in
285 particle aggregation. Initially, particles were aggerated together to various extents, but upon
286 shearing, the interactions between particles were broken and structures were similar. The
287 flow curve of 0.2% LA was different at higher shear rates, where it appears to shear thicken
288 at ~50 s^{-1}, this was likely due to the larger aggregates jamming in the geometry. The
289 viscoelastic behaviour of the fluid gels was measured using oscillatory rheological data
290 (Figure 4b). At LA concentrations up to 0.1%, the loss modulus (G'') dominated over the
291 storage modulus (G') indicating a more viscous response from the system. However, at
292 0.15% and 0.2% LA, G' was dominant, which reflects a more elastic response. These
293 structures also exhibited a yield stress. Therefore, as aggregation of the particles increased
294 due to increased surfactant binding, a network with gel-like properties began to form,
295 leading to an eventual dominance in G'.



296

297 *Figure 4: (a) shear viscosity of 1 wt% κC fluid gel mixed with LA at 0.025% (□), 0.05% (○), 0.075% (△), 0.1% (▽), 0.15%*
298 *(◇) and 0.2% (×). (b) storage modulus (□) and loss modulus (■) of 1 wt% κC fluid gel mixed with LA as a function of LA*
299 *concentration.*

3.3 Surface activity

The functionality of LA as a surfactant depends on its ability to adsorb at the a/w interface, lowering the surface tension and stabilising the newly formed interface. In order to investigate the surface-activity of κC-LA complexes, equilibrium surface tension was measured and compared to that of pure surfactant solutions (Figure 5). The surface tension of pure LA solution decreased with concentration reaching a plateau at 0.15% LA with a value of 34.6 ± 0.07 mNm^{-1}. This is therefore its critical micelle concentration (CMC); above this concentration, all additional surfactant monomers added to the system form micelles. The surface tension of the complexes were then measured as a function of LA concentration and compared to the pure surfactant solutions. The surface tension of pure kappa carrageenan was 43.4 ± 0.3 mNm^{-1} (Figure 5). Upon addition of LA, the surface tension quickly began to decrease until it plateaued at 35.0 ± 0.6 mNm^{-1} at 0.025% LA. It then appeared to increase slightly at 0.1% LA. This is thought to be a result of the formation of aggregates affecting the measurements. Above 0.1% LA, the aggregates increased in size resulting in unreliable measurements. In surfactant-particle systems, the surface tension is often lower than that of corresponding surfactant solutions [41]. It has been suggested that particles act as surfactant carriers, thus increasing the concentration of surfactant at the a/w interface [7] and that the size of the particles (dependent on individual systems) determines the extent to which the surface tension is lowered [42]. Particle-surfactant systems here exhibited similar surface tension values to the surfactant solutions (Figure 5). The aqueous conditions, as well as size and shape of the particles may have therefore not been optimal to cause a lowering of surface tension.

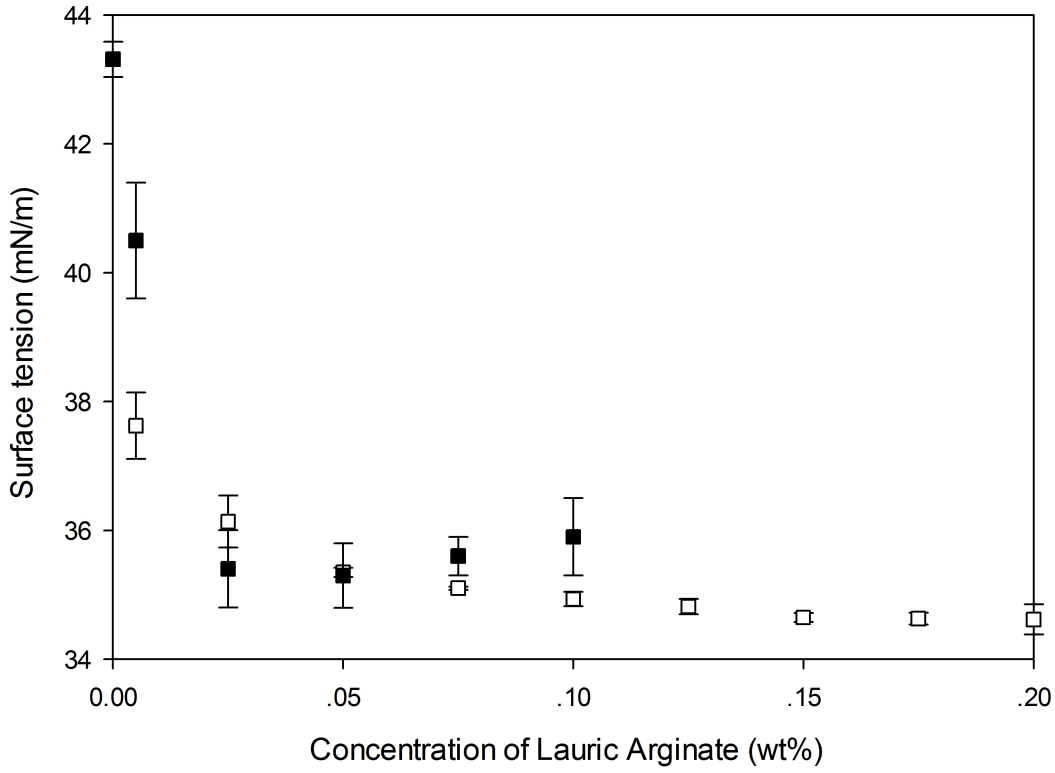


Figure 5: Surface tension measurements as a function of LA for pure LA solutions (□) and κC-LA complexes (■).

3.4 Aeration of surface-activated kappa carrageenan fluid gels

The ability of κC-LA complexes to incorporate air was determined using foam air fraction measurements and compared to those of pure surfactant solutions. Systems were aerated in a Hobart mixer for 7 minutes, which ensured that the air fraction was high. The air fraction of pure surfactant solutions quickly reached a constant of around 0.97 upon increasing LA concentration (Figure 6a). Foam capacity was high above and below the CMC suggesting the method of foaming allowed equilibrium surface tension to be reached. The air fraction of aerated κC-LA complexes followed a similar trend but values were slightly lower than those of the pure surfactant solutions (~ 0.86). This was likely a result of increased viscosity preventing the incorporation of as much air into the system. In addition, Lesov, Tcholakova [43] have reported that foam air volume is also dependent on the mechanism of stabilisation as well as solution viscosity, specifically the Pickering stabilised foams they studied had a lower air fraction when compared to surfactant-stabilised foams

of similar suspension viscosities. At 0.15% and more substantially, 0.2% LA, the air fraction decreased. This was likely an effect of high particle aggregation and increased particle density, as observed by turbidity and rheology measurements, which sterically hindered the action of the surfactant. In addition, it was likely dense particles bridged and consequently ruptured bubble interfaces as they were generated, preventing the growth of the foam structure.

In order to investigate the potential Pickering stabilisation action of newly-formed κC-LA complexes, foam stability was explored. Firstly, foam half-life was measured and compared to those of pure surfactant solutions (Figure 6b). Foams produced at 0.005% and 0.2% LA were not measured as the air fraction was too low. Foam half-life initially increased from 35 $\pm$ 3 h at 0.025% LA up to 61 $\pm$ 8 h at 0.075% LA, where it peaked before decreasing to only 12 $\pm$ 2 hours at 0.15% LA. All systems were stable for considerably longer than foams composed of pure surfactant solutions, which were only stable for 1.5 – 4 hours (Figure 6b). A similar trend in foam stability is often seen for particle-surfactant systems where the most stable foam corresponds to the optimum ratio of particle to surfactant concentration [5, 8, 44]. This is where particles are coated with a surfactant monolayer resulting in their lowest charge and maximum hydrophobicity. Foam stability then decreases due to the formation of a surfactant bilayer on the particle surface rendering them hydrophilic and resulting in the mechanism of stabilisation changing from particle-stabilised to surfactant-stabilised. This explanation does not justify the peak in foam stability observed here, as the ζ-potential data (Figure 2) revealed that a bilayer did not form on the surface of particles at high LA concentrations as particles remained negatively charged. To investigate the trend observed

here, the position of the particles in the foams was explored, as well as the rate of coarsening and liquid drainage.

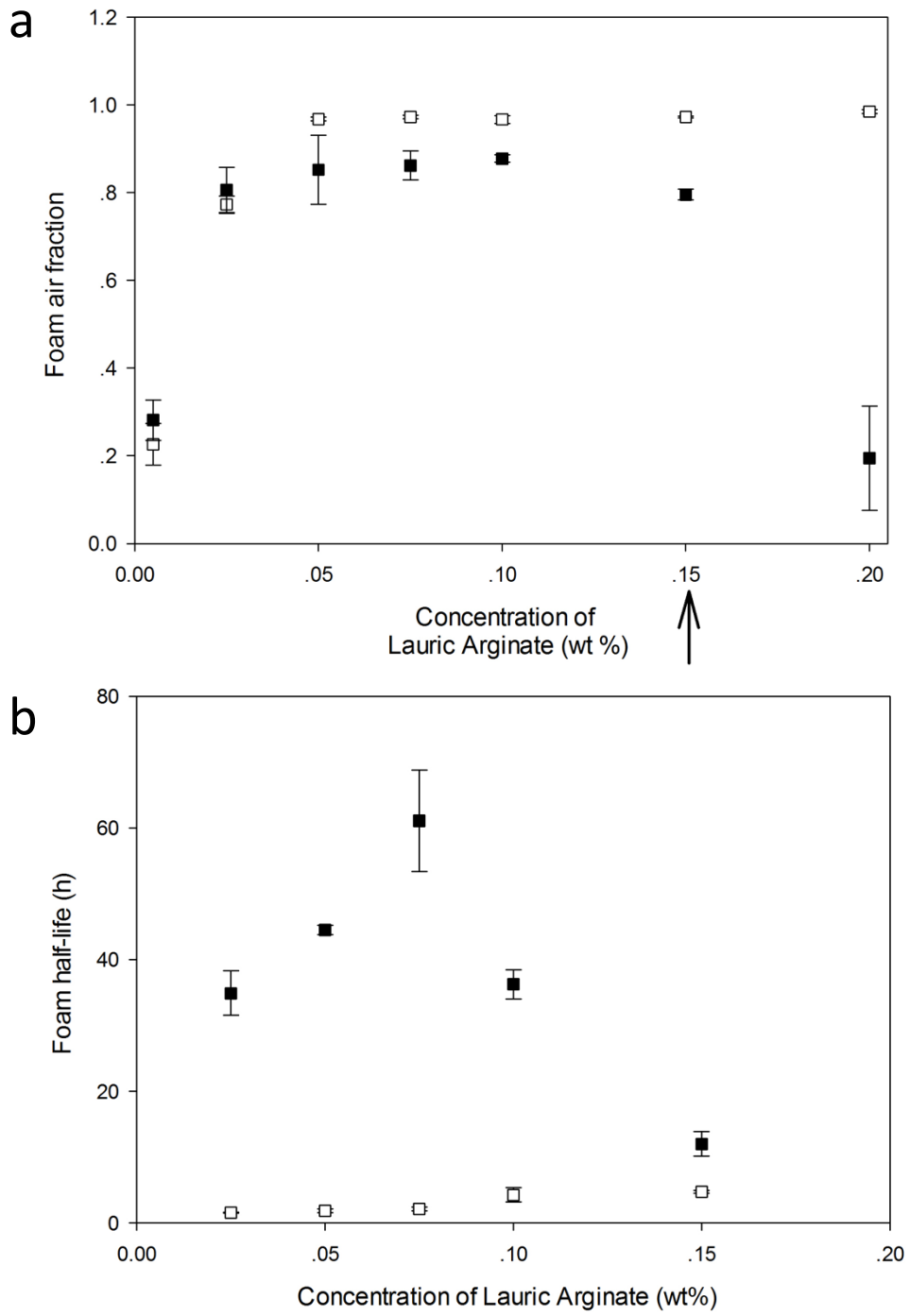


Figure 6: (a) foam air fraction measurements for aerated κC-LA complexes (■) and pure LA solutions (□), as a function of LA concentration. Arrow indicates the CMC of LA. (b) foam half-life measurements for aerated κC-LA complexes (■) and pure LA solutions (□), as a function of LA concentration.

3.5 Foam stability mechanism

Firstly, the location of particles in the foams was examined using optical and confocal microscopy to investigate the surface-activity of the modified κC particles. The bubbles formed upon aerating pure LA solutions were also imaged for comparison; these bubbles were spherical with smooth interfaces (Figure 7a). In contrast, foams produced with κC-LA complexes (at all LA concentrations) consisted of bubbles that appeared non-spherical and had a structured surface (Figure 7b). This is indicative of bubbles stabilised by adsorbed particles [8]. The micrograph in Figure 7c of aerated κC with 0.075% LA further supports this, as a layer of particulate entities can be seen at the surface of bubbles with tails protruding into the continuous phase. Both micrographs (Figure 7b and Figure 7c) also demonstrate the presence of particles in the continuous phase that had not adsorbed to the interface. The particles appeared quite different to those imaged in Figure 1a before complexation and aeration (longer and thinner in shape), it is possible that they deformed to increase their efficiency of adsorption at bubble interfaces. To provide further information on the coverage of bubble interfaces, confocal microscopy was used. Particles were dyed with rhodamine B and appear green in the micrographs (Figure 7d). A layer of particles can be seen on bubble interfaces providing high coverage. Particles can also be seen in the continuous phase. Microscopy was used to study all aerated complexes; some adsorption of particles at bubble interfaces was seen in all cases, verifying the ability to surface-activate κC particles through surfactant binding. However, it was difficult to quantify the magnitude of particle coverage using microscopy. Therefore, the change in bubble size over time was studied to analyse the effectiveness of particle coverage.

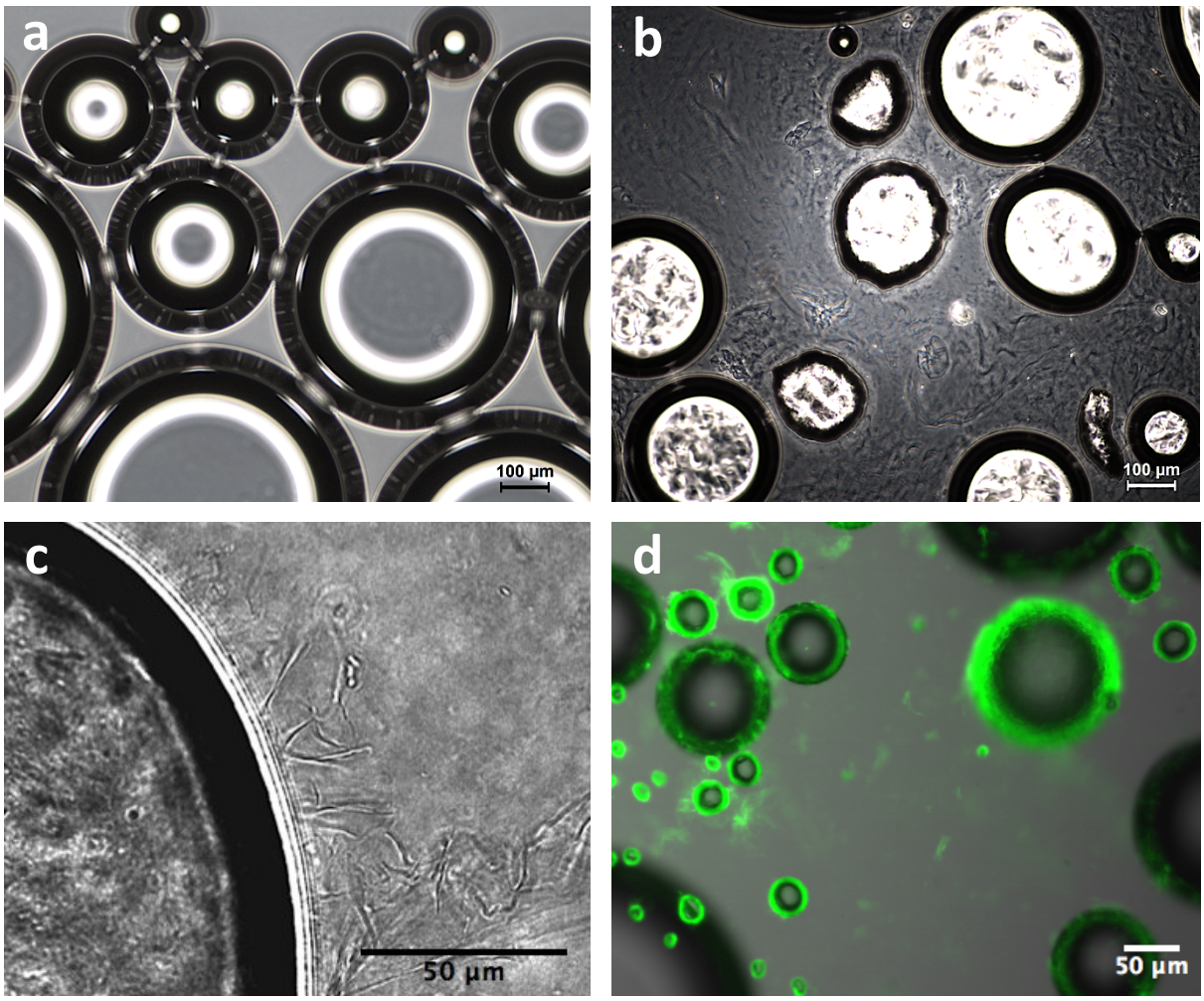


Figure 7: (a) optical micrograph of aerated 0.2% LA solution. (b) optical micrograph of aerated 1 wt% κC + 0.075% LA fluid gel complexes. (c) optical micrograph of aerated 1 wt% κC + 0.075% LA fluid gel complexes at a higher magnification. (d) confocal micrograph of aerated 1 wt% κC + 0.075% LA fluid gel complexes dyed with rhodamine B.

It has been well reported that particles adsorbed to a/w interfaces provide a barrier to coarsening of the gas phase [3, 22]. The structure of these foams including bubble size over time was therefore recorded using a high resolution camera. Mean bubble area as a function of time for the first 4 h after aeration was plotted for each foam (Figure 8a). The initial mean bubble area (MBA) was similar for all foams (~7000 μm^2), which corresponds to a bubble radius of ~12 µm. The MBA increased with time in all cases, due to disproportionation. This is where smaller bubbles shrink in size and larger bubbles grow due to the difference in their internal Laplace pressure. The foam consisting of κC particles and

403 0.025% LA displayed the highest rate of disproportionation (MBA ~ 70000 μm^2 after 4 h).
404 Upon increasing LA concentration to 0.05% and 0.075%, the smallest increase in MBA was
405 observed (~20000 μm^2 after 4 h) and upon further increasing LA to 0.1% and 0.15%, the rate
406 of disproportionation subsequently increased again (~40000 μm^2 after 4 h). These changes
407 in disproportionation rates suggest differences in interfacial viscoelasticity, perhaps caused
408 by a difference in stability mechanisms. It appears that at the lowest concentration of LA
409 (0.025%), the foam is surfactant stabilised and therefore more vulnerable to
410 disproportionation. At 0.05 and 0.075% LA, there is sufficient surfactant to coat the surface
411 of the particles and foams are consequently particle stabilised. The interfacial viscoelasticity
412 is high and the interface is protected against disproportionation. Above 0.075%, the rate of
413 disproportionation begins to increase again. This suggests a change in dominant stability
414 mechanism from particle stabilised to surfactant-stabilised. This cannot be due to the
415 formation of a surfactant bilayer and consequent change in particle charge as is common
416 with these systems (discussed in Section 3.4). It is therefore possible that there was a
417 barrier to adsorption for some of the particles. Deleurence, Parneix [37] studied the effect
418 of particle aggregation by de-coupling the effects of ζ-potential and particle charge (i.e. they
419 varied the sign of the ζ-potential without changing the contact angle over a large rage of
420 surfactant concentration). They found that foam properties were controlled by the
421 flocculation state and the shear energy applied to produce the foam. Large aggregates did
422 not adsorb spontaneously at the interface because of their size, however, when large shear
423 energy was used to produce the foams, a very stable foam was formed. Adsorption of
424 particles occurs if the time for adsorption, t_A is considerably less than the time for interface
425 creation, t_{CR}. Both times depend on shear energy but the ratio does not. The ratio t_A/t_{CR}
426 scales as a/d, where a is the diameter of the particles and d is the diameter of the bubbles.

Large aggregates in the order of 100 μm could therefore not adsorb as t_A/t_{CR}=10. The size of bubbles in this study were initially ~ 12 μm (Figure 8a). Therefore when aggregates reached ~ 120 μm in diameter, adsorption would have been hindered. Above 0.075% LA, aggregates greater than 100 μm in size were observed by optical microscopy, which continued to increase in size with LA concentration (as discussed in Section 3.2). These would have been unable to adsorb to the interface, which explains the trend seen in Figure 8a. The interface would have been stabilised by free surfactant monomers, as well as those particles small enough to adsorb (the number of which would have decreased with increasing LA concentration).

As well as particles being present at a/w interfaces, microscopy highlighted their presence in the continuous phase i.e. foam channels and nodes. Liquid drainage of the bulk phase was therefore measured to assess how it related to foam stability. Liquid content, calculated using conductivity data, is shown for each foam after 4 h as a fraction of initial content (Figure 8b). The trend is similar to that observed for foam half-life. The particle stabilised foams (0.05% LA and 0.07% LA) displayed little change in liquid content after 4 h. Whereas, a decrease was measured for 0.025%, 0.1% and 0.15% LA (surfactant-stabilised foams). This demonstrates that when particles adsorbed to the interface, their resistance to liquid drainage as well as disproportionation increased. In addition, the interaction and aggregation between particles would have helped to strengthen this barrier through the formation of a particle network between air bubbles [7, 42, 45]. However, when foams were surfactant stabilised, the classical drainage equation is applicable [46, 47]. Despite higher viscosity of the continuous phase upon increasing LA concentration (Figure 4), the liquid drainage was controlled by the change in stability mechanism.

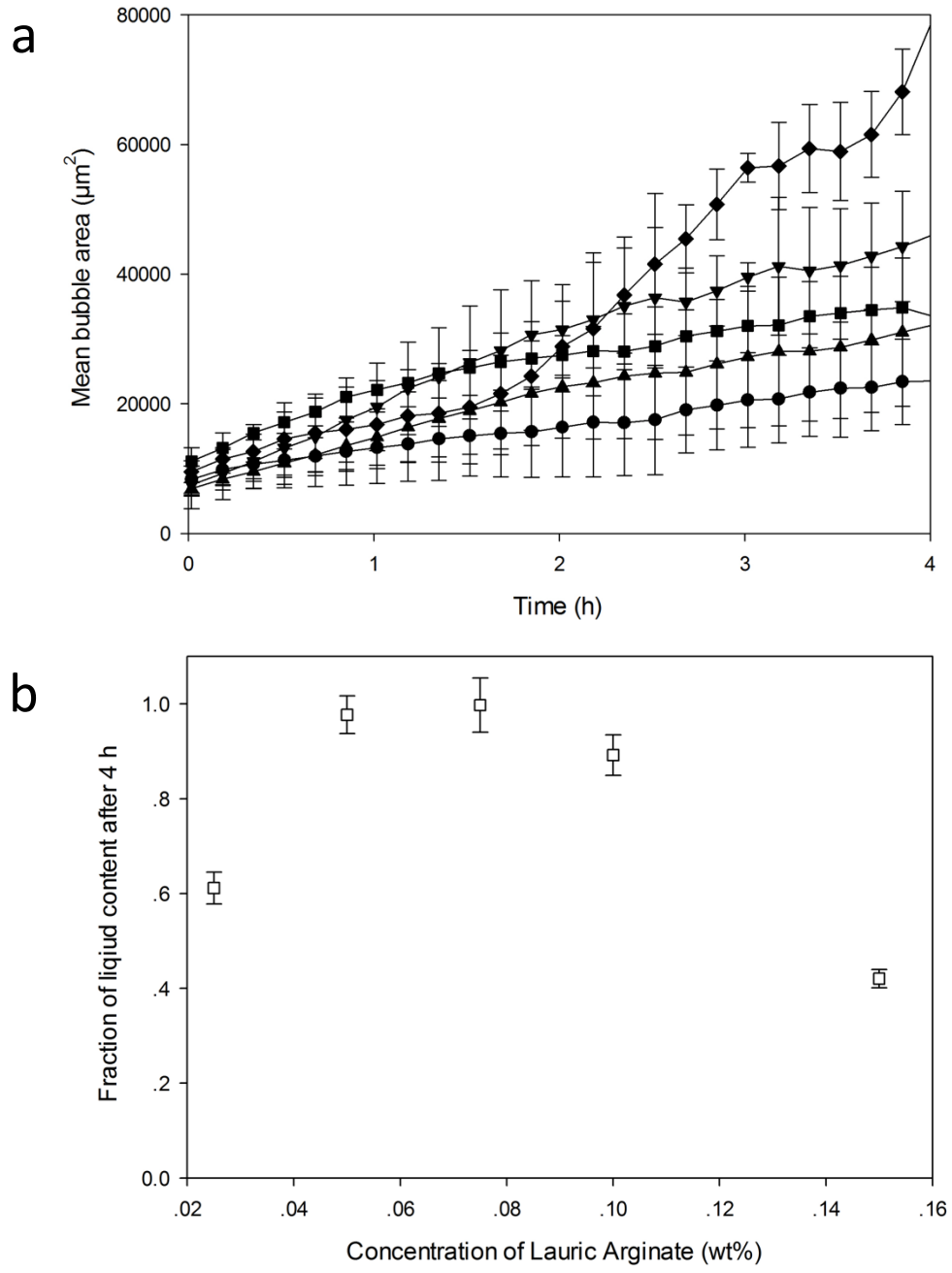


Figure 8: (a) mean bubble area of aerated κC-LA complexes as a function of time after aeration, LA concentrations of 0.025% (◆), 0.05% (●), 0.075% (▲), 0.1% (▼) and 0.15% (■). (b) fraction of liquid content remaining 4 h after aeration in aerated κC-LA complexes as a function of LA concentration. Measurements were recorded at sensor 3 in a Krüss foam column (positioned half way down the foam).

3.6 κC fluid gels with non-ionic surfactant

In order to confirm this change in surface-activity of kappa carrageenan upon binding to LA, the foaming properties of kappa carrageenan mixed with a non-ionic surfactant, Tween 20, were studied. Following the same procedure as LA, a diluted 1% κC fluid gel was prepared and mixed with Tween 20 at various concentrations. Firstly, their ability to incorporate air

461 was determined using foam air fraction measurements and compared to pure surfactant
462 solutions (Figure 9a). As the CMC of Tween 20 is quite low (0.0074 wt% [48]), which is
463 typical of non-ionic surfactants, it was used at concentrations above this in order to increase
464 foamability. The foam air fraction of pure surfactant solutions increased with Tween 20
465 concentration until it plateaued at around 0.98 (Figure 9a). Foam air fractions of κC and
466 Tween 20 mixed solutions followed a similar trend but, as with κC and LA fluid gel solutions,
467 they were slightly below those of pure Tween 20 due to increased viscosity. Foam half-lives
468 were then measured and plotted as a function of Tween 20 concentration in Figure 9b. No
469 increase in stability was observed upon addition of κC to Tween 20 solutions; both systems
470 were stable for only 1-4 hours at all concentrations. In addition, the bubbles were spherical
471 and non-textured (Figure 9b inset), confirming that there was no adsorption of particles at
472 the interface or interaction between κC and Tween 20.

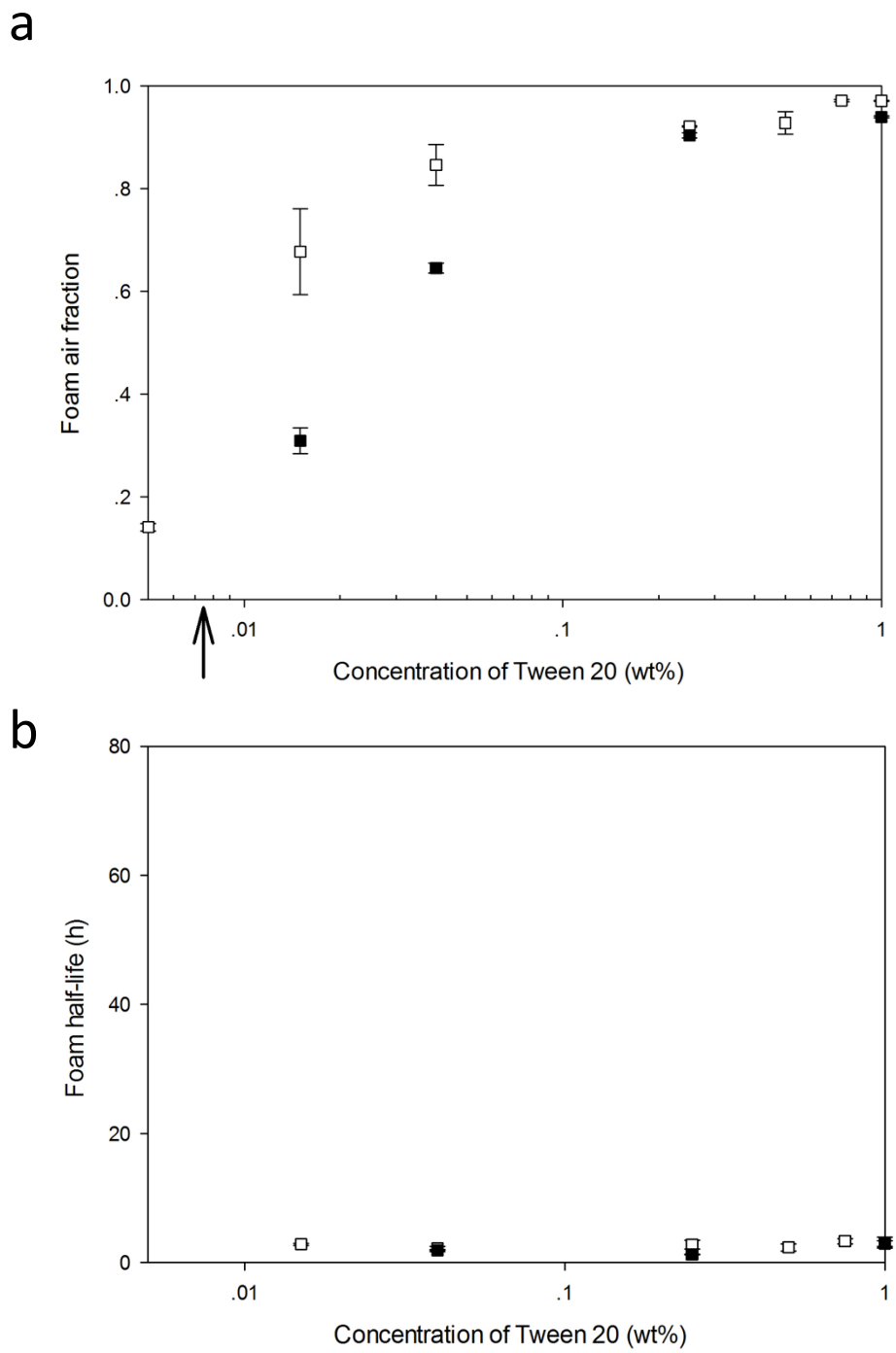


Figure 9: (a) Foam air fraction measurements and (b) foam half-life measurements for 1 wt% κC + Tween 20 fluid gel complexes (■) and pure Tween 20 solutions (□), as a function of Tween 20 concentration. Arrow in (a) indicates the CMC of Tween 20. (b) inset is an optical micrograph of aerated 1 wt% κC + 0.075% Tween 20 fluid gel.

4 Conclusions

This research has built upon work by Bonnaud, Weiss [24] who characterised an electrostatic interaction between food-grade cationic surfactant, lauric arginate, with negatively charged carrageenan in solution but did not explore their surface properties or ability to stabilise the a/w interface. In this work, the electrostatic interaction was facilitated between microgel particles of kappa carrageenan and LA. Turbidity, ζ-potential and rheological measurements were used to characterise the complexes, in particular their aggregation behaviour, which showed similar patterns to those observed by Bonnaud, Weiss [24]. The ability of complexes to lower surface tension was similar to that of pure surfactant solutions, however foams were over 10 times more stable in all cases. Foam half-life peaked at an intermediate concentration of LA (0.075% LA). This peak was attributed to a change in stability mechanism from surfactant stabilisation to particle stabilisation, where the most stable foams exhibited a smaller increase in mean bubble size over time (slower disproportionation rate), as well as a slower liquid drainage rate. The adsorbed particles therefore provided sufficient interfacial elasticity to considerably slow these mechanisms, helped also by the interaction and aggregation between particles. However, at higher LA concentrations, extensive aggregation limited their ability to adsorb to the interface and foam stability decreased as surfactant stabilisation once again dominated. Similar particle-surfactant systems have been limited by the formation of a surfactant bilayer on the surface of particles, changing their hydrophobicity [5, 8, 44]. A surfactant bilayer did not form in this system, suggesting that by optimising the size of particles and aggregates, greater foam stability can be reached.

This work helps to expand the existing knowledge of *in-situ* modification of hydrophilic particles for foam stabilisation, in particular work by Binks, Muijlwijk [14] who extended this method to the food industry. To the best of the authors' knowledge, this is the first time that a surfactant has been used to surface-activate kappa carrageenan particles facilitating their adsorption to a/w interfaces. This provides a simple method to functionalise one of the most commonly used polysaccharides in the food industry, providing a more versatile ingredient for food microstructure design. For example, these particles have the potential to mimic fat droplets in whipped products, in terms of both texture and their role in stabilising the structure. There are many exciting future directions to further explore the knowledge gained in this study. For example, the optimisation of microgel shape and size may allow more efficient adsorption at the interface further increasing foam stability; Murphy, Farkas [28] reported the ability of smaller microgel particles to adsorb to an interface and increase interfacial elasticity more quickly. A more consistent shape and size may also allow the adsorption kinetics and structure at the interface to be more thoroughly investigated. In addition, the potential surface-activation of other polysaccharides (anionic and cationic) with other surfactants should be explored to utilise this efficient method of modification.

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