Stabilizing bubble and droplet interfaces using dipeptide hydrogels

Citation for published version:
Avino, F, Matheson, A, Adams, D & Clegg, P 2017, 'Stabilizing bubble and droplet interfaces using dipeptide hydrogels', Organic & Biomolecular chemistry. https://doi.org/10.1039/C7OB01053B

Digital Object Identifier (DOI):
10.1039/C7OB01053B

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published in:
Organic & Biomolecular chemistry

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Stabilizing bubble and droplet interfaces using dipeptide hydrogels

Fernando Aviño,* Andrew B. Matheson,† Dave J. Adams,* and Paul S. Clegg*‡

Hydrophobic dipeptide molecules can be used to create interfacial films covering bubbles and droplets made from a range of oils. At high pH, the dipeptide molecules form micelles which transform into a hydrogel of fibres in response to the addition of salt. We characterize the properties of the hydrogel for two different salt (MgSO₄) concentrations and then use these gels to stabilize interfaces. Under high shear, the hydrogel is disrupted and will reform around bubbles or droplets. Here, we reveal that at low dipeptide concentration, the gel is too weak to prevent ripening of the bubbles; this then reduces the long-term stability of the foam. Under the same conditions, emulsions prepared from some oils are highly stable. We examine the wetting properties of the oil droplets at a hydrogel surface as a guide to the resulting emulsions.

Introduction

Proteins have been used by cooks to stabilize foams and emulsions for many centuries. The proteins are typically trapped on the interface and can denature, especially at liquid/air interfaces. By comparison, small peptides can potentially improve performance in two diametrically opposed ways. (1) Isolated small peptides will be adsorbed to the interface more quickly which can aid bubble or droplet formation. This tends to be the more challenging route. (2) These small molecules may self-assemble into larger structures which retain their order at the interface; the trapping at the interface can be much stronger than for individual proteins. Proteins have also been used as subunits within robust composite particles which themselves are interfacially active. Nonetheless, short peptide sequences offer the distinct advantages of ease of synthesis and design as well as the tendency to self-assemble at very low concentration.

Recently, the behaviour of very short peptide sequences at liquid/air interfaces has begun to be explored. Here naphthalene-protected diphenylalanine (2NapFF) molecules have been investigated most. One approach was to investigate the self-assembly of the dipeptide at the air/water interface prepared via drop-casting. A thin interfacial film formed from a dispersion of 2NapFF at high pH on contact with a low-pH subphase. FTIR and pH variation tests show that this self-assembly behaviour is associated with the carboxylic acid group of the dipeptide becoming rapidly protonated at the interface. The film was made up of self-assembled fibres and behaved like an elastic sheet. The same dipeptide (2NapFF) also formed a hydrogel via the addition of metal ions. This hydrogel can be used to stabilise aqueous foams for weeks. The dipeptides at 1 wt% concentration self-assemble into fibre-like networks at both, the air/water interface and in the bulk. The same dipeptide sequence (Fmoc-FFF) also formed a hydrogel via the addition of metal ions. This hydrogel can be used to stabilise aqueous foams for weeks. The dipeptides at 1 wt% concentration self-assemble into fibre-like networks at both, the air/water interface and in the bulk. Raman spectroscopy hinted at a possible change in the balance between π-stacking and hydrogen bonding, with the latter appearing to drive self-assembly close to the interface. The dipeptide concentration as well as the type and concentration of metal ions, affects the foam stability. When the bulk hydrogel had a yield stress larger than the Laplace pressure of the bubbles, ripening was suppressed.

Separately, the stabilization of emulsions using di-, tri- and hepta-peptides has also been investigated. Initial experiments showed that it was possible to stabilize chloroform droplets for months using an interfacial network of dipeptide fibres. Here the dipeptide sequence was protected by N-((fluorenlyl-9-methoxy)carbonyl) (Fmoc) with self-assembly being driven by π-stacking and hydrogen bonding. The fibres were self-assembled nanostructures and, for a well-chosen dipeptide sequence, remained stable in the presence of added salt or when the temperature was raised. Curiously, using the tri-peptide sequence Fmoc-FFF it was possible to stabilize water droplets in chloroform, demonstrating the importance of the hydrophobicity of the fibres. Unprotected tripeptide emulsifiers divided into two classes: those that self-assembled into fibres prior to adsorption and those that adsorbed to droplets as a single-molecule layer. The former were more effective at stabilizing droplets of rapeseed oil. As an alternative demonstration of the key role played by self-assembly, an Fmoc protected dipeptide sequence, Fmoc-tyrosine-leucine (FmocYL) was used as a switchable emulsifier.
An enzyme was employed to cleave a phosphate group which was initially attached to the tyrosine group. With the phosphate group attached chloroform droplets are stable for less than an hour; by contrast, when emulsification is carried out in the presence of the enzyme, the dipeptide self-assembles into nanofibres which then stabilize the emulsion for months.\(^8\) These studies strengthen the claim that it is the fibres which are most effective at stabilizing the liquid interfaces and not the separate molecules. Very recently a seven peptide molecule has been designed to self-assemble into fibres with excellent surfactant properties.\(^9\) At this length, the short peptide sequence has properties which are robust to changes in some parts of the sequence. Even more recently a low molecular weight gelator has been synthesized at a water-oil interface to create stable droplets which can be induced to coalescence by a trigger.\(^15\)

The formation of bulk hydrogels by our dipeptide of choice, 2NapFF (Figure 1a), has been studied in great detail.\(^16\)–\(^18\) Gelation can be induced by initially dispersing the molecule at high pH and then adding salt or lowering the pH. Alternatively, the 2NapFF can be dispersed in dimethyl sulphoxide (DMSO) and then subsequently this can be diluted with water. While the gel strength does not change significantly for these different routes, the microstructure and yielding behaviour do alter.\(^18\) When gelation is triggered by the addition of salt (here Ca\(^{2+}\)), the system exhibits a significant sensitivity to the initial high pH chosen which may be due to the differing degrees of lateral association between micelles. Further studies have shown that the use of divalent cations (Mg\(^{2+}\), Ca\(^{2+}\)) leads to the formation of hydrogels with higher storage and loss moduli than monovalent cations (Li\(^+\), Na\(^+\), K\(^+\)). The choice of anion has some additional effect on the moduli. These experiments also suggested that worm-like micelles always preceded salt-induced hydrogelation.\(^16\) More recently, a subtler relationship has been revealed: at high pH, 2NapFF self-assembles into spherical micelles above a first cmc of 0.01 wt\%, with worm-like micelles are found above a second cmc of 0.07 wt\%.\(^17\) At around 1 wt\%, the worm-like micelles are found to aggregate. Typically addition of the calcium salt transforms worm-like micelles into hydrogels. However, above the first cmc, there appear to be structural transformations that occur on addition of the calcium salt, which allows gels to form in this intermediate regime. This is the concentration regime that we focus on here.

In this Paper, we outline the route to hydrogel formation induced by MgSO\(_4\) at low 2NapFF concentration (0.1 wt\%). We then use this hydrogel to stabilize foams and emulsions. Our results show that using a low concentration of dipeptide and Mg\(^{2+}\) rather than Ca\(^{2+}\) undermines the stability of the foam compared to previous observations.\(^7\) By contrast, it is possible to create highly stable emulsions based on several different oils. We separately characterize the wetting behaviour of the oils and a bubble at a hydrogel interface. We consider the stability of our composites in the light of the wetting character of the hydrogel film at the fluid-fluid interface.

### Results and Discussion

In order to investigate foams and emulsions, the underlying hydrogels need to be repeatably produced. For this reason, we carefully studied the process of dispersing and gelling the dipeptide (see Experimental section). Whether and how long it takes for a gel to form and its ultimate properties are affected by factors such as pH, temperature, ionic strength and mechanical shear rate.\(^16\)–\(^19\) A thorough study of the effect of temperature on dispersions of 2NapFF has been published very recently.\(^21\) Here, we compared the use of an ultrasound bath with a magnetic stirrer and found that the former resulted in more transparent dispersions. Dipeptide dispersion and gelation times initially differed between ostensibly identical hydrogels prepared using the ultrasonic bath presumably due to the \(\pm 8^\circ\text{C}\) variation in the bath temperature. For this reason, we established two temperatures (\(< 35^\circ\text{C}\) and \(50^\circ\text{C}\)) for dispersing the dipeptide. The rate of dipeptide dispersion (unsurprisingly) and the subsequent gelation time (unexpectedly) was found to be faster for the hydrogels prepared...
at 50°C compared to those prepared at < 35°C. Our final protocol was to place the sample in an ultrasonic bath (at a controlled temperature) for 0.5 h until a translucent slightly viscous solution was formed, Figure 1b.

By leaving dispersions (prepared using either ultrasound or a magnetic stirrer) to stand for 24 hours at a room temperature (22°C), we found that self-supported gels, able to pass the inversion vial test, sometimes formed (see Figure 1c,d). Structural transitions, linked to increases in viscosity, have been observed before in 2NapFF dispersions which have been warmed in the temperature range of our bath (albeit at higher concentration). These changes in organization can then become trapped.22 We suggest that we might be seeing similar behaviour here. To avoid this, all of our hydrogels were prepared by the addition of salt within 5 minutes of removal from the ultrasound bath. Figure 1e,f demonstrates how the temperature of the ultrasound bath influences the speed of subsequent behaviour. Dipeptide dispersed at 50°C has begun to gel within two minutes of the addition of salt. Typical hydrogels for two difference concentrations of MgSO₄ are shown in Figure 1g,h.

The evolution of shear modulus was measured (see Experimental section) as a function of time to study the strength of hydrogels prepared at 18 mM and 142 mM MgSO₄ (Figure 1i). G' and G" of hydrogels with high salt concentration rise faster than hydrogels with low salt concentration within the first 10,000 seconds. At this point, G' and G" of hydrogels with high salt concentration hardly increase, reaching their maximum at 6 kPa for G' after a few thousand seconds, while G' and G" of low salt concentration hydrogels continue to increase even after 63,000 seconds. Salt induced gelators which become weaker at higher salt concentration have been seen previously. The strength of a hydrogel prepared at 0.5 wt% of 2NapFF and Ca²⁺ salt was found to reach its maximum value at a concentration of 2:1 Ca²⁺ to dipeptide. Increasing further the concentration of Ca²⁺ resulted in weaker gels.16

Figure 2a,c shows foams formed from dispersions prepared at < 35°C which were gelled with 18 mM and 142 mM MgSO₄, respectively. The formation method is described in the Experimental section. Foams with low salt concentration (Figure 2a) resulted in higher-quality foams with small average bubble size and a higher volume of liquid entrained in the foam compared to those prepared at a high salt concentration (Figure 2c). The bubble size is often related to foam stability due to the enhanced buoyancy of large bubbles; however, in this case we find that after 0.5 h it is the foam with smaller bubbles that has collapsed more, Figure 2b,d. Evidently, while these hydrogels provides a good environment for creating bubbles the interfacial layer and sparse bulk gel are unable to prevent rapid coalescence. This is especially true with small bubbles which consume a greater proportion of fibres as the interfacial layer.

Fluorescence confocal microscopy was carried out to try to understand the foam performance. Figure 2e shows the organization of a fresh foam prepared at 142 mM MgSO₄ and 50°C. The nanofibers prefer to adsorb at the air/aqueous interface (similar to ref. 23) rather than being dispersed in the continuous phase, Figure 2e. However, over the next hour hydrogel begins to

Fig. 2 Illustrates fresh foams (a,c) and foams after 0.5 hours (b,d) prepared from 2 mM 2NapFF and dispersed at < 35°C; (a,b) 18 mM MgSO₄ and (c,d) 142 mM MgSO₄. (e) Shows a confocal micrograph of a fresh foam prepared at 2 mM 2NapFF, 142 mM, MgSO₄, and dispersed at 50°C. Dipeptides are dyed using Nile Blue; scale bar 100 μm.

Fig. 3 Fourier Transform Infra Red absorbance data for a dispersion of 2NapFF and foams made at the two salt concentrations. There is a very significant growth in the peak around 1650 cm⁻¹ corresponding to the formation of random coil structure.
emerge between bubbles. This is very much reminiscent of the foams reported in ref.7 which were created at significantly higher dipeptide concentration and gelled using CaCl2. In that work, the hydrogel initially formed on the bubble interfaces but then steadily appeared between the bubbles but now over a timescale of days rather than tens of minutes. At our very low concentrations of the dipeptide the foam lifetime is only two hours, indicating that the remnant hydrogel between the bubbles is now too weak to prevent coalescence and ripening.

As we have found changes in hydrogel properties depending on the ultrasound bath temperature, we repeated the same series of measurements starting from a dispersion made at both temperatures. No changes were observed. By contrast, using CaCl2 rather than MgSO4 to create the foam did lead to enhanced stability. With the calcium salt neither varying the salt concentration (15 mM and 120 mM) nor varying the initial ultrasound bath temperature, altered the foam properties noticeably. We conclude that any residual influence of the ultrasound bath temperature is negated once the rotor stator has been used to destroy the initial hydrogel. When the fibres re-form on the surface of the bubbles, the detailed properties of gelator system can remain influential.

In order to examine the organization of the molecules we have used FTIR, Figure 3, for a dispersion of 2NapFF (black), a foam prepared at low salt concentration (red) and a foam prepared at high salt concentration (blue). The samples were allowed to dry prior to characterization. The original dispersion has a peak at 1630 cm\(^{-1}\), which may reflect the intermicellar order. No peak was observed at 1720 cm\(^{-1}\), indicating that the carboxylic acid group is deprotonated. A peak appears at 1650 cm\(^{-1}\) once salt has been added and grows with increasing salt concentration. This may well be related to the formation of a random coil structure, although we highlight that it is difficult to assign these dipeptides on the basis of conventional IR data.

Emulsions with four different oils (isopropyl myristate, silicone oil, dodecane, octanol) were prepared in a similar manner to the foams described above. Three out of four emulsions remained stable for months (Figure 4a,c,e). Isopropyl myristate emulsions (Figure 4a) appeared the most ideal in that there was no creaming. At the other end of the range, octanol emulsions (Figure 4g) could not be stabilised, phase separating immediately after preparation. Indeed it appears that the dipeptide material occupies the small volume of oil phase at the top of the sample and this plug floats above water, Figure 4i. Less surprisingly, a small amount of creaming occurred within the first hour for silicone oil (Figure 4c) and dodecane (Figure 4e) emulsions. The volume of the clear aqueous phase in these emulsions barely increased after months. The same set of measurements were repeated at 50°C and 142 mM MgSO\(_4\) and at < 35°C, 18 mM and 142 mM MgSO\(_4\) for each of the oils. The emulsification performance and stability are broadly similar.

Confocal images of the emulsions are presented in Figure 4b,d,f,h. Here, the dipeptides show a preference for the oil phase in the following sequence: octanol (3.4) > isopropyl myristate (3.3) > silicone oil (2.6) > dodecane (2). The numbers in brackets are the dielectric constants. Self-assembled dipeptides in isopropyl myristate emulsions (Figure 4b) show a clear preference for the interfaces. The concentration of dipeptide in the aqueous phase increases slightly for silicone oil emulsions (Figure 4d) and further still for the dodecane emulsions (Figure 4f). The octanol samples are comprised of some sparse aqueous droplets within a background of dipeptide in the oil phase (Figure 4h). This unexpected behaviour is consistent with our observations of the macroscopic emulsion, Figure 4g,i.

It is tempting to consider the role of the interfacial dipeptide fibres to be similar to the interfacial particles in a Pickering emulsion.24 Under this scenario, whether the dipeptide fibres become trapped at the interface depends on their wettability by the two fluid phases. To explore this idea we have carried out an experiment to observe the wetting behaviour of the oils1 at an interface between the hydrogel and an aqueous phase of the same salt concentration, Figure 5a. If the hydrogel surface was precisely horizontal and reasonably flat we would be able to use the angle with which the droplet or bubble meets the hydrogel surface (measured through the aqueous phase) as a quantitative measurement of the wettability of the hydrogel. Unfortunately, since the surface is somewhat rough it is not possible to be quantitative. The air and the dodecane appear to make approximately similar (small) angles to the hydrogel surface (Figure 5c,d). This suggests that in both cases the hydrogel greatly prefers contact with the aqueous phase over contact with the droplet / bubble. By contrast, isopropyl myristate makes a more gentle angle with the surface of the gel, Figure 5b. The preference of the hydrogel for contact with the aqueous phase is significantly less marked, this is consistent with the formation of a stable emulsion. If the behaviour of octanol, described above, was because of the wetting characteristics of this oil at a hydrogel surface then we would expect

\[\text{We have not considered the behaviour of the silicone oil because it is density matched with the aqueous phase and hence does not rise to meet the hydrogel interface.}\]
foams become less stable at low dipeptide concentration. The fibre behaviour is found to be closely similar to that at higher concentrations but evidently the gel structure is now too weak. By contrast, we have been able to form long lived emulsions using three out of the four oil phases that we have tested. Here the droplets could be stabilized by an interfacial film (isopropyl myristate) or by hydrogel both in the aqueous phase and on the interface (dodecane and silicone oil). The oil which could not be emulsified in this way (octanol) could not be described simply using the wetting characteristics of the hydrogel. This observation warns against a simple comparison between the behavior of these self-assembled fibres and the particulate emulsifiers used in Pickering emulsions. The new process, not observed in Pickering emulsions, is that some components partition into the oil phase but apparently not the intact fibres which are preferentially wet by the aqueous phase.

**Experimental**

**Hydrogel preparation**

2NapFF was synthesised as described previously. All chemicals were purchased from Sigma-Aldrich and Fisher Chemicals and used as received. Vials and instruments were cleaned with hexane, followed by methanol and rinsed with ultra pure water before use. An equimolar quantity of NaOH (1 M, aq) was added to millipore water (resistivity = 18.2 MΩcm) to give a basic solution (pH 11±0.5). Then 2 mM 2NapFF was added and the mixture was dispersed. Ultimately this was carried out using an ultrasound bath (VWR model USC 300 T with power 80 W). The pH was 11±0.5 measured with a Seven Easy pH probe (Mettler Toledo AG).

Gelation was triggered by adding MgSO₄·7H₂O or CaCl₂·2H₂O aliquots on top of the translucent dispersion. The form of addition matters. By adding the salt already dissolved, hydrogels are more homogeneous compared to those prepared by adding the salt as a powder. It is possible that the latter favours the formation of two phase samples. In practice, all samples were prepared using 0.1 wt% dipeptide and were gelled using pre-dissolved salt to give a 1 mL sample. This was then left to stand for 12 h at room temperature before use in subsequent experiments.

**Foam and emulsion preparation**

Foams were prepared from the gels by using a rotor stator homogeniser (Polytron, PT-MR 3100) with a 12 mm diameter head, operating at 15,000 rpm (shear rate ≈ 25,700 s⁻¹) for 50 seconds. Immediately following foam formation, the samples were sealed with parafilm to prevent liquid evaporation; the height of the foam was recorded as a function of time.

Emulsions with four different oils (isopropyl myristate, silicone oil, dodecane, octanol) were prepared in a similar manner to the foams described above. In each case 200 µL of the oil was placed on top of the hydrogel prior to high-shear mixing.

**Rheology**

Initial tests for gelation were performed by vial inversion. Oscillatory shear measurements, were conducted on a TA Instru-

---

**Conclusions**

Following previous studies stabilizing emulsions and foams using dipeptide hydrogels, we have investigated the behaviour of one dipeptide system at low concentration with the gelation induced by the addition of salt. We have presented a route to achieving repeatable gel formation based on the dipeptide 2NapFF and using the salt MgSO₄. Using this gel system we have demonstrated that
ments AR 2000 rheometer with cross-hatched parallel plates with 40 mm diameter and 1.0 mm gap distance. A 4 mL (0.1 wt%) dispersion solution of the dipeptide was previously prepared in a 7 mL glass vial, as described above. Gels were triggered on the bottom plate of the rheometer by loading the 4 mL dispersion and adding 18 mM MgSO$_4$ for hydrogels with low salt concentrations and 142 mM MgSO$_4$ for hydrogels with high salt concentration. The sides of the plates were covered with low viscosity mineral oil to avoid water evaporating from the hydrogel. Gelation process was observed by measuring the shear modulus (storage modulus G’ and loss modulus G”) as a function of time at a frequency of 1 Hz and at a constant strain of 0.5% for a period of ~18 hours. Experiments were carried out at 22°C.

Confocal microscopy
The measurements were carried out by using a Zeiss AxioObserver.Z1 inverted microscope and a Zeiss LSM 700 scanning system 9 with a 20× (0.40 NA) objective. Nile Blue at a concentration of 0.55 mM was used to label the dipeptides; this was excited using a 633 nm semiconductor laser.

FTIR
IR spectra were measured using a Smiths Illuminat IR module coupled to a Renishaw inVia Raman microscope. Each spectrum was scanned between 4000 and 650 cm$^{-1}$ and corrected for the influence of the optics and the substrate.

Contact angle
The hydrogel (blue) was created, using our standard protocol, in the base of a sample vial in the presence of Nile blue dye. Following gelation, additional salt solution was added above the hydrogel. This two-phase cell was then inverted with the use of a petri dish. A droplet of oil or a bubble of air was added using a syringe with a U-shaped needle, Figure 5a.

References
1. S. Damodaran, Journal of Food Science, 2005, 70, R54–R66.
2. G. G. Scint, P. J. McKnight, T. Turtle and R. V. Ulijn, Advanced Materials, 2016, 28, 1381–1386.
3. A. F. Dexter, A. S. Malcolm and A. P. J. Middledge, Nature materials, 2006, 5, 542–506.
4. A. F. Dexter and A. P. J. Middledge, Journal of Physical Chemistry C, 2007, 111, 10484–10492.
5. S. Bai, C. Pappas, S. Debnath, V. W. C. Lai, E. D. Leibler, F. Jiang and R. V. Ulijn, Advanced Mater, 2014, 26, 7005–7013.
6. T. Li, M. Kalloudis, A. Z. Cardoso, D. J. Adams and P. S. Clegg, Langmuir : the ACS journal of surfaces and colloids, 2014, 30, 13854–13860.
7. T. Li, F. Nudelman, J. W. Tavao, J. Vass, D. J. Adams, A. Lips and P. S. Clegg, Advanced Materials Interfaces, 2016, 3, 1500601.
8. I. P. Moreira, J. R. Sansell, D. A. Cannon, M. Hughes, D. A. Lamprou, T. Turtle and R. V. Ulijn, Soft matter, 2016, 12, 2629–2631.
9. S. Mondal, M. Vareenik, D. N. Bloch, Y. Atsmon-Raz, G. Jacoby, L. Adler-Abramovich, L. J. Shimon, R. Beck, Y. Miller, O. Regev and E. Gazit, Nature Communications, 2017, 8, 14018.
10. J. T. Russell, Y. Lin, A. Roker, L. Su, P. Carl, H. Zettl, J. He, K. Sill, R. Targarola, T. Emrick, R. Littrell, P. Thyagarajan, D. Cookson, A. Pery, Q. Wang and T. P. Russell, Angewandte Chemie - International Edition, 2005, 44, 2420–2426.
11. L. Isa, J.-M. Jung and R. Mezzenga, Soft Matter, 2011, 7, 8127.
12. A. Ye, X. Zhu and H. Singh, Langmuir, 2013, 29, 14403–14410.
13. M. Sarkar, N. Tomczak and S. Lim, ACS Applied Materials & Interfaces, 2017, 9, 11193–11201.
14. Z. Gao, J. Zhao, Y. Huang, X. Yao, K. Zhang, Y. Fang, K. Nishinari, G. O. Phillips, F. Jiang and H. Yang, DRT - Food Science and Technology, 2017, 76, 1–8.
15. Y. Nishida, A. Tanaka, S. Yamamoto, Y. Tominaga, N. Kunikata, M. Mihuhta and T. Maruyama, Angewandte Chemie International Edition, 2017, in press.
16. L. Chen, G. Pont, K. Morris, G. Lotze, A. Squires, L. C. Serpell and D. J. Adams, Chemical communications (Cambridge, England), 2011, 47, 12071–3.
17. A. Z. Cardoso, L. L. E. Mears, B. N. Bloch, P. C. Griffiths, R. Schweins and D. J. Adams, Soft Matter, 2016, 12, 3612–3621.
18. C. Calipho, E. Draper, R. Schweins, M. Marcellino, L. Serpell, D. Vadukul and D. Adams, Soft Matter, 2017, 13, 1914–1915.
19. J. Shi, Y. Gao, Y. Zhang, Y. Pan and B. Xu, Langmuir, 2011, 27, 14425–14431.
20. L. Chen, T. O. McDonald and D. J. Adams, RSC Advances, 2013, 3, 8714.
21. D. J. Adams, E. Draper, H. Su, C. Braemat, R. Poole, S. Rogers, H. Cui and A. Seddon, Angewandte Chemie International Edition, 2017, in press.
22. A. Z. Cardoso, Personal Communication.
23. K. G. Alagoresu, D. S. Warhadpande, V. N. Puzyrov and O. D. Velev, Langmuir : the ACS journal of surfaces and colloids, 2004, 20, 10371–4.
24. B. P. Binks, Current Opinion in Colloid & Interface Science, 2002, 7, 21–41.
25. L. Chen, S. Revel, K. Morris, L. C Serpell and D. J. Adams, Langmuir : the ACS journal of surfaces and colloids, 2010, 26, 13466–71.