

RSC Advances

Long-term stabilization of reflective foams in sea water

Journal:	RSC Advances
Manuscript ID:	RA-ART-08-2014-008714.R1
Article Type:	Paper
Date Submitted by the Author:	29-Sep-2014
Complete List of Authors:	Evans, Julian; UCL, Chemistry Hailes, Helen; UCL, Chemistry Ward, John; University College London, Department of Biochemical Engineering Aziz, Alex; UCL, Chemistry

SCHOLARONE[™] Manuscripts

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012,

Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Long-term stabilization of reflective foams in sea water

Alex Aziz,^a Helen C. Hailes,^a John M. Ward,^b Julian R.G. Evans^a

This work explores the challenge of making persistent foams in salt water to provide high reflectance. While stable foam is essential in the food industry and in fire fighting, this is the first work aimed at combining foam persistence with reflectance. One application is the use of oceanic foams to increase planetary albedo: extending foam lifetime moderates the energy required to maintain large areas of 'ocean mirror'. Two compositions to produce such foams in seawater are described. The first is based on high methyl ester pectin-type A gelatin complexes which produced foams with a reflectance of ~0.5. The second produces stable foams using cellulose ethers and iota carrageenan gelling agents. These foams gelled in the presence of sea water to give measured reflectance of 0.65 - 0.75. Both had lifetimes, without wave action, beyond three months at which point the experiment ended. In contrast, single protein species such as gelatin B, whey protein isolate and albumin produced short-lived foams. Foam stability was measured by recording liquid drainage and foam height as a function of time. In the event that climate interventions are needed, such additives would be appropriate for nutrient-deficient ocean regions that support low levels of marine life.

Introduction

The role of proteins in stabilising foams for food processing has been widely studied¹⁻³ as have applications in fire fighting⁴ which has spawned a huge patent literature. Similarly polysaccharide/carbohydrate polymers have played an increasing part in food production and drug delivery⁵. In this work, we approach the putative application of similar non-toxic materials to increase oceanic albedo. Climate engineering seeks to manage incoming solar radiation^{6,7} and is the only intervention that can be implemented rapidly⁸. An increase in the earth's albedo from 0.15 to 0.17 would balance a forcing⁷ of 4 Wm⁻² corresponding to atmospheric CO₂ levels of 550 ppm. While not changing CO₂ levels, this could mitigate the health⁹ and security¹⁰ problems identified with global warming irrespective of its causation.

Two groups have proposed increasing oceanic albedo using scattering from multiple air-water interfaces^{11,12}. Whitecaps are natural foams produced when ocean waves break and have a reflectance of 0.4– 0.6 in the visible spectrum and 0.1 at 2 μ m¹³. They contribute to global energy balance but are short-lived. An ocean mirror strategy would extend their coverage and effect. The ocean albedo is only 0.05 except at high solar zenith angles¹⁴. Interventions to albedo may have much greater effects than attempts to modify atmospheric composition¹⁵ and could certainly be implemented quickly⁸.

The energy required to create an 'ocean mirror' from surface foam, even if sourced from wind or wave energy devices is considerable so the strategy is only viable if extended foam lifetime, above ~ 2 Ms is possible. Over 20% of the world's oceans contain limited marine life due to lack of iron. These high nutrient low chlorophyll regions¹⁶ where iron deficiency limits the algal growth needed to support a marine ecosystem, provide the most suitable locations.

Foams can be classified as dry or wet depending on their liquid content, wet foam having liquid content >20% with spherical cells whereas in dry foams, the cells form polyhedra¹⁷. Both increase diffuse reflectance of the ocean. Simplification in predicting the reflectance of foams is provided by Stabebno and Monahan's¹⁸ conjecture that the reflectance of a foam could be directly related to the number of rafts and is independent of bubble size, except possibly for fine bubbles, validated for multiple layers of glass plates¹⁹. Thus foam of about 10 rafts delivers a reflectance of 0.5.

Trace amounts of fatty acids in the ocean originate from anthropogenic and biogenic sources²⁰ but proteins can have high aqueous solubilities, are degraded by bacteria present on the ocean surface²¹ and

can be designed to sink to the ocean floor after degradation. They stabilize foams by increasing surface viscosity of the liquid film²² acting as a barrier to coalescence and foam ripening^{23,24}, modifying steric interactions through interaction of positive and negatively charged groups^{22,25} and by acting as filler particles to increase viscosity²⁶. Gelatin is made up of hydrolysed collagen polypeptide chains which undergo hydrophilic and hydrophobic interactions below 21 °C (10% solution)²⁷.

We describe here our recent results on foam persistence in water and salt water of (i) protein solutions; albumin, whey protein isolate (WPI), gelatin type A and gelatin type B, (ii) proteins with pectin gelling agents (high (HM) and low methyl ester (LM)) and (iii) combinations of cellulose ethers and iota carrageenan gum.

Experimental Details

Hydroxypropyl methyl cellulose (HPMC), (E50 FG) was kindly donated by Dow Chemical Co. UK, iota carrageenan (GP379) by Gelcarin FMC Biopolymers, Bournal, Beligum, pectins B-3887 and B-3887 by CP Kelco, Lille Skensved, Denmark. Type A gelatin from porcine skin (G1890) 50,000 – 100,000 g mol⁻¹, type B gelatin from bovine skin (G9391) 50,000 – 100,000 g mol⁻¹ , ovalbumin (A5253) 44,300 g mol⁻¹ and barium sulfate 99% were bought from Sigma-Aldrich company Ltd, Dorset UK. Seamix (natural sea water mixture) was bought from Peacock salt, Scotland. Whey Protein Isolate (WPI) (90%) 18,400 gmol⁻¹ was from Wholefoods Online, Kent, UK.

A du Noüy Torsion Balance (White Electrical Instrument Co. Ltd. UK) fitted with a platinum ring 40 mm in circumference was used for surface tension measurements. After each measurement, the platinum was washed with distilled water and heated in a blue Bunsen flame. The surface tension of distilled water was measured before and after each sample and the glass dish cleaned eight times using distilled water. Each solution was tested six times. Distilled water was taken directly from the glassware of the still. A comparison of surface tension was made between distilled water and sea salt solution at 35.2 g Γ^{1-28} .

A Philips HR2020/50 Compact Blender (400 W) was used on setting 2. Solutions of 200 ml were foamed for 1 minute, sufficient to reach a maximum foam capacity²⁹. This is hereafter designated 'food mixer method'. In some cases, a glass tank measuring 108 x 102 x 300 mm³ fitted with a Makita 650 W electric drill with a metal stirrer attachment was used: hereafter designated 'stirrer method'. Foam stability was measured by recording foam volume and liquid drainage as a function of time^{30,31}. Surfactant solutions were prepared in both sea water and distilled water at 1 wt.% gelatin type A, gelatin type B, WPI (Whey protein isolate) and albumin. Binary mixtures were 0.5 wt.% gelatin Type A mixed with 0.05, 0.2, 0.35, 0.5 wt.% HM Pectin and with the same fractions of LM Pectin. HPMC (1 g) was dissolved in 100 ml distilled water by slow addition at room temperature with continuous stirring. Iota carrageenan (0.1, 0.2 and 1 g) was dissolved in 100 ml distilled water heated to 70 °C. These solutions were left overnight to ensure complete dissolution. They were foamed for 60 s in the food mixer while adding equal volumes of 70.4 gl-1 sea salt stock solution to give a final salt concentration of 35.2 gl⁻¹.

The hydrophobicity of proteins was correlated with protein amino acid sequences³² obtained from the NCBI protein database. Each amino acid is given a hydrophobic score and the average hydrophobicity is found from the total hydrophobicity divided by the total number of amino acid residues.

Laser methods are unsuitable for reflectance measurements of foams because they are too localised and the integrating sphere needs modification for liquids but the 0°/45° arrangement is an ideal and accepted geometry for diffuse reflectance measurement³³. A 0°/45° diffuse reflectance instrument was constructed from a Gnome Alphax Major slide projector (Cardiff UK) with a 300W Hanimex bulb adjusted to create a parallel beam and positioned 0.2 m from a 45° mirror. Diffuse reflected light was measured using a BPW 41N photodiode shunted with a 470 Ω resistor arranged at an angle of 45° in such a way that the ray diagram constructed for the rays entering the detector tube originated from an ellipse well within the illumination circle on the sample. Measurements were recorded Multimeter 1705 (Thurlby using а Thandar

Instruments). All readings were referenced to a slip-cast barium sulfate disc having 97% reflectance over the visible spectrum ³⁴.

WPI, albumin, Type A gelatin and Type B gelatin were tested individually for their foaming capacity using 600 ml of 1 wt.% solutions using the stirrer method. The effect of temperature and seasalt on 1 wt.% WPI was investigated by analysing foam stability in distilled and sea water at room temperature and after standing at 60 °C for 4 hours, a temperature chosen to allow unfolding of the protein but not covalent denaturing³⁵.

The LM and HM pectin – gelatin solutions were made up as follows. HM pectin was slowly added to 200 ml of 35.2 gl⁻¹ sea water at 75 °C with vigorous stirring and left for 15 hours before reheating to 50 °C and stirring for 1 hour while type A gelatin was dissolved. After cooling to ambient temperature, foaming was done using the food mixer method. In contrast, LM pectin was initially added slowly to 100 ml distilled water at 75 °C while stirring and then allowed to stand for 15 hours. It was reheated to 50 °C to allow gelatin to be added while stirring for 1 hour and cooled. Foaming, using the food mixer method was then done while adding 100 ml of 70.4 gl⁻¹ sea salt stock solution bringing the salt composition to 35.2 gl⁻¹.

Viscosity measurements were carried out using a UKAS certificated reverse flow Cannon-Fenske viscometer supplied by Rheotek following the procedure of BS188:1977. Solutions where left for 4 hours at room temperature before testing. The viscometer was cleaned using distilled water and acetone and dried at 60 °C. A water bath was set to 25 °C (± 0.1 °C) using a thermoregulator (Techne TE-10A, Stafford, UK) driving against a water-cooled copper

coil. A BSI certificated mercury-in-glass thermometer (0.1 °C) was used to monitor temperature. A time delay of 15 minutes was given to allow the sample to reach the equilibrium temperature of 25 °C before removing the filling syringe and measuring the flow time.

Results and Discussion.

Foaming method

Although microbubbles (<100 μ m dia.) can be prepared by sonication, frit and disc generation and microfluidics, such foams require higher volumes of surfactant: in proportion to their surface area to volume ratios. Coarser polydisperse foams were therefore sought. While there is much literature on foam stability, even at times up to 18 ks ^{25,26,29-31,36-40}, the prospect for extended salt-water foam lifetime is a new objective. Three methods were tested for foam generation. Compressed air using nozzles produced large bubbles (5-10 mm) irrespective of nozzle diameter and was abandoned. The food mixer method was quick and effective, producing fine polydisperse foam (1-5 mm cells). The stirrer method produced slightly finer cells (~1 mm).

Protein foaming without gelling agents

The foaming capacity of Albumin, WPI, gelatin type A and gelatin type B is shown in Table 1 along with surface tension, protein molecular weight and hydrophobicity calculated from the hydrophobicity index. High hydrophobicity and lower surface tension confer foaming capability²⁹ but the minor differences did not correlate well with these parameters. One advantage of gelatin type B over WPI may be its linear fibre-like structure²⁷, allowing the gelatin molecules to

Table 1. Foaming capacity of protein surfactants expressed as initial foam volume, V_0 (1 wt.% in distilled water), initial surface tension, γ_{SV} (95% confidence limits from a 't' distribution) and average hydrophobicity per residue, H_{AV} (Cysteine Residues) (That of gelatin was calculated based on the average number of amino acids over 1000 residues²⁷. * β -lactoglobulin was used for calculations for WPI as it is the major constituent.) Experiments were repeated 6 times on 600 ml volumes.

Protein Surfactant	V ₀ / ml (±10 ml)	γ _{SV} / mN m ⁻¹	95% C.L / mN m ⁻¹	H _{AV}
Albumin	1,180	46.8	1.4	28.65 (6)
WPI *	920	45.0	1.3	27.33 (5)
Gelatin (Type A)	1,030	59.9	1.3	-2.04 (0)
Gelatin (Type B)	1,100	54.8	0.6	-1.78 (0)

unfold more easily compared to WPI with its 3-D structure. Gelatin also has no cysteine residues which form covalent disulfide bridges restricting reorientation³⁸.

Foaming of type A and B gelatins was similar despite the hydrophobicity score. A factor not taken into account is the molecular weight distribution of type A and type B gelatin which can result from different degrees of peptide hydrolysis during extraction: type A generally has a wider distribution²⁷.

Drainage volume against time (Figure 1) produces 'drainage half life', (time taken for half initial volume to drain) which is an indication of foam stability³¹ although this can be misleading as shown below. All these proteins drained half of their initial 200 ml liquid volume within 360 s. Maximum drainage was not seen within 900 s in gelatin type A or albumin. WPI and gelatin type B were both unstable in the salt solution with complete foam collapse after 400 s.



Figure. 1 Liquid drainage of foamed protein surfactants in sea water (200 ml volume) (● albumin; ■ whey protein isolate; ▲ gelatin type A; ◆ gelatine type B)

Albumin produced the most stable foam with the lowest drainage rate of 0.8 ml s⁻¹ and the longest drainage half life of 228 s ($R^2 = 0.991$) although after 900 s the rate of drainage was still ~0.1 ml s⁻¹. The drainage half life of the gelatins was calculated using non-linear regression analysis to be 100 s ($R^2 = 0.992$) and 105 s ($R^2 = 0.991$) for type A and B respectively. Gelatin type A produced the interesting result that rate of drainage decreased drastically after 900 s, an effect missed by half-life determination. This could be due to re-orientation of the type A gelatin as well as the progress of gelation over time. In contrast, complete

liquid drainage and foam collapse occurred after 400 s when gelatin type B was foamed in sea water.

Gelatin type A has a pI of 8-9 and is positively charged at neutral pH. Gelatin type B has a pI of 4.8 -5.5 and is negatively charged at neutral pH²⁷. Chatterjee and Bohidar⁴¹ suggest that charged electrolytes like NaCl screen electrostatic interactions between charged sites on gelatin molecules. As gelatin type B has a reduced charge, less interaction would take place leading to a decrease in stability.

In all cases, the foams produced thus far would not be sufficiently stable to support an 'ocean mirror'.

Following the experiments of Ryan et al.³⁹ showing that foam stability of WPI increased when heated in a 108 mM NaCl solution, WPI was heated for 4 hours at 60 °C in a seawater solution before foaming using the food mixer and the foam volume collapse was followed. The results (Figure 2(a)) show that when WPI was denatured

by heating in seawater there was significantly increased foam lifetime. WPI denatures at higher temperatures exposing hydrophobic regions. Gelatin is able to gel at low temperatures. There is potential scope for further investigation of protein composition widening the potential sources of protein for this application.



Figure. 2(a). Mean foam volume for 1% WPI in seawater and in distilled water at room temperature and at 60 °C. Error bars reflect measurement error of ± 5 ml. (♦ heated in seasalt solution at 60 °C for 4 hours; ■ in distilled water at 20 °C; ▲ in seasalt solution at 20 °C; x heated in distilled water at 60 °C for 4 hours)



Figure. 2(b). Volume of drained liquid for 1% WPI in seawater and in distilled water at room temperature and at 60 °C. Error bars reflect measurement error of ± 5 ml. (\blacklozenge heated in seasalt solution at 60 °C for 4 hours; \blacksquare in distilled water at 20 °C; \blacktriangle in seasalt solution at 20 °C; \checkmark heated in distilled water at 60 °C)

Figure 2(b) shows the corresponding drainage curves. Drainage continued but a stable foam upper layer was preserved. The drainage curves tend to provide less discrimination between foam-producing compositions. Denaturing WPI in distilled water had no effect on stability as measured by foam volume: collapse closely follows the curves for un-denatured WPI. Denaturing WPI exposed hydrophobic regions which were able to produce more stable films. The issue still remained that drainage was the main factor in foam collapse and the best WPI foams lasted for only 7.2 ks. This is also consistent with results of Ryan et al.³⁹ who measured liquid half life over a period of 150-350 s. A step change is needed: the approach was to explore the addition of gelling agents for their putative contribution to stabilization.

Protein with pectin gelling agents

Pectin, a naturally occurring polysaccharide has the ability to polymerise into a macromolecular gel which reduces foam drainage through increased viscosity²⁶. Pectins are divided into two types depending on the degree of esterification (DE) of the galacturonic acid groups with high methyl ester (HM) pectin having DE>50% and low methyl ester (LM) pectin having DE<50%. LM pectin requires divalent cations and temperatures below 60 °C for gelation depending on DE ⁴². Electrostatic interactions between the cations and negatively charged carboxylic acid groups mean that pectin increases foam stability through increased viscosity and gelation. FT-IR estimated the DE for LM and HM pectins as 11% and 85% respectively, close to the manufacturer's values of 7% and 71%.

Solutions of 1 wt.% low or high methyl ester pectins alone did not foam in either distilled water or seawater. Surface tension measurements at 1 wt.% for the LM pectin were (62.0 ± 1.6) mNm⁻¹ (95% C.L. n=6) and for the HM pectin (70.4 ± 0.6) mNm⁻¹ (95% C.L. n=6), not greatly reduced from the surface tension of distilled water. Contemporary measurements of distilled water were within 0.5% of the quoted value of 72 mNm⁻¹ ^{1 43}. Pectin alone was thus confirmed not to produce foams this way in agreement with Schmidt *et al.*²⁶.

Low methyl ester (LM) Pectin

LM pectin would not dissolve in sea water at the 0.5 wt.% level at 75 °C because divalent cations provide gelation conditions, total divalent cation content being 1.70 gl⁻¹. LM pectin solutions were made up in distilled water and salt concentration (35.2 gl⁻¹) adjusted during foaming. This produced rapid gelation and stable foam. Table 3 gives the reflectance measurements for the gels.

LM pectin can be dissolved in salt water above its gelation temperature $(90 \text{ }^{\circ}\text{C})^{44}$ which would require onboard solar heating tubes if performed on ocean platforms.

 Table 3. Liquid drainage after 4 hours from gelled LM pectin - gelatin type A foams in seawater. Reflectance was calculated against a barium sulfate standard Experiments were repeated 3 times and a 95% interval was calculated from a t-distribution.

	Drainage / ml	Reflectance
0.05 wt.% LM pectin - 0.5 wt.% type A gelatin	130±25	0.77±0.04
0.20 wt.% LM pectin - 0.5 wt.% type A gelatin	77±14	0.76±0.04
0.35 wt.% LM pectin - 0.5 wt.% type A gelatin	50±25	0.69±0.06
0.50 wt.% LM pectin - 0.5 wt.% type A gelatin	23±14	0.66±0.06

High Methyl ester (HM) Pectin

Figure 3 shows the results of liquid drainage of a foamed solution of 0.5 wt.% HM Pectin against time in the presence of 0.5 wt.% type A or type B gelatins. Initial drainage occurred at a rate of ~ 0.5 mls⁻¹ in all

solutions with complete foam collapse occurring in the 0.5 wt.% HM pectin-0.5 wt.% type B gelatin within 3 hours. The drainage rate decreased after about 4 minutes and a maximum of 170 ml drained from the initial 200 ml solution. The remaining 30 ml was a stable foam

over the course of the experiment conducted over 12 weeks.

Such extraordinary stability may arise as the gelatin type A is positively charged and interacts with the negatively charged HM pectin. The time delay permits initial drainage as gelation progresses. The seemingly indefinite stability of these foams in the laboratory highlights the way in which a foam drainage

experiment can be misleading. The drainage was high initially but gelled foam is persistent and lasted months. The formation of electrostatic interactions between HM pectin and gelatin type A is supported by Farris *et al.*⁴⁵ who showed a reduction in swelling of a 13 wt.% gelatin type A-1 wt.% LM pectin hydrogel by about 7-fold compared to hydrogels produced with 14 wt.% gelatin.



Figure. 3. Mean liquid drainage against time of gelatin type A, gelatin type B, HM Pectin foamed with gelatin type A and HM Pectin foamed with gelatin type B in sea water. Error bars indicate standard error plus error in measuring liquid drainage (±5 ml).(♦ 0.5 wt.% HM pectin – 0.5 wt.% type A gelatin; ● 0.5 wt.% HM pectin – 0.5 wt.% type B gelatin; ▲ 0.5 wt.% gelatin type A; x 0.5 wt.% gelatin type B; ▼ gelatin type A; ∎ gelatine type B).

Addition of 0.35 wt.% HM pectin (instead of 0.50 wt.%) to 0.5 wt.% gelatin type A produced seawater foam of similar stability with a maximum drainage of 170 ml over the course of two weeks. Addition of 0.05 wt.% HM Pectin resulted in a foam that completely drained over 4 days. A seawater solution of 0.5 wt.% gelatin type A alone completely drained over a period of 24 hours.

Foams prepared from 0.2-0.5 wt.% HM pectin-0.5 wt.% gelatin type A had a reflectance of 50-54%. This is comparable to measurements of albedo of ocean whitecaps.

Methylcellulose - iota Carrageenan Solutions

Carrageenans are polysaccharides derived from red seaweeds⁴⁶. Gelation occurs in the presence of cations by an end to end double-helix association⁴⁷. Methylcellulose is thermogelling from 42.5 °C ⁴⁸ due to increased interactions of hydrophobic units and showed no difference in liquid drainage in salt or distilled water, confirming data from Xu *et al.* ⁴⁹.

At 0.5 wt.% iota carrageenan-0.5wt.% methylcellulose solution in distilled water persistent foam was produced with maximum drainage rate of 0.02 ml s⁻¹ (Figure 4). Below 0.5 wt.% iota carrageenan



foams were unstable. Figure 5 shows the morphology of a methyl cellulose-carrageenan foam in sea water.

Figure. 4. Foam volume of methylcellulose - iota carrageenan solutions in distilled water against time (♦ 0.5 wt.% iota carrageenan gum – 0.5 wt.% methyl cellulose; ■ 0.1 wt.% iota carrageenan gum – 0.5 wt.% methyl cellulose; ▲ 0.5 wt.% methyl cellulose in seawater; × 0.5 wt.% methyl cellulose in distilled water).



Figure. 5. A methyl cellulose-carrageenan foam originally made in sea water: after they are dry, the foams persist as solids indefinitely.

Dissolving iota carrageenan in sea water below 75 °C was impeded by gelation induced by the presence of cations^{44,47}. The viscosity of 0.1 wt.% iota carrageenan was higher ($8.7 \text{ mm}^2\text{s}^{-1}$) in seawater than in

distilled water (4.1 mm²s⁻¹). Gobet *et al.*⁴⁴ have shown that a 1 wt.% solution of iota carrageenan began gelation with added salt concentrations as low as 0.06 mol 1^{-1} . This is the reason the foams were produced while blending salt and salt-free solutions. These carrageenan-methyl cellulose solutions produced stable foams with most bubbles in the region of 1 mm or below and a reflectance of 0.65-0.75. On the other hand the HM pectin - type A gelatin foams produced larger bubbles of several 5 mm in diameter and reflectance of between 0.5-0.55.

The use of iota carrageenan in ocean foaming may require dissolving it at 90 °C to avoid gelation conditions⁴⁴ which could be feasible using on-board solar heating tubes but would limit the duty cycle to daylight hours. It is clear that more investigation of these and similar systems is needed. This work has not investigated the engineering aspects of delivery of oceanic foams because the first logical step is to identify a viable foam with appropriate properties and to establish achievable lifetimes.

Viscosity measurements

Kinematic viscosity measurements are reported in Table 4. Accuracy is confirmed by measuring distilled water and prepared sea water solution giving 0.90 and 0.93 mm²s⁻¹ for distilled and sea water respectively. These compare to the literature values of 0.89 mm² s^{-1 43} and 0.95 mm² s^{-1 50} respectively (Errors 0.5% for

distilled water and 1.4% for sea water). The results in Table 4 show that at lower concentrations of HM pectin, viscosity in sea water is suppressed compared to distilled water. The reason is likely to be that the salt solution inhibits aggregation of the pectin. As the HM pectin concentration increased to 0.50 wt.% the salt ions may then be unable to inhibit aggregation.

Table 4. Viscosity measurements of HM pectin and gelatin type A solutions in distilled and sea water	c. (95% confidence
intervals n=3).	

Solution	Kinematic viscosity /mm ² s ⁻¹ 95%C.L.	
	Distilled water	Sea water
Solvent 0.5 wt.% Gelatin type A 0.05 wt.% HM pectin 0.2 wt.% HM pectin 0.35 wt.% HM pectin 0.50 wt.% HM pectin 0.05 wt% HM pectin+0.5wt.% gelatine A	0.9±0.01 2.80±0.08 1.54±0.01 3.10±0.01 4.91±0.08 9.58±0.09 -	$\begin{array}{c} 0.93 \pm 0.01 \\ 2.16 \pm 0.01 \\ 1.21 \pm 0.02 \\ 2.75 \pm 0.02 \\ 5.36 \pm 0.11 \\ 10.40 \pm 0.20 \\ 2.17 \pm 0.02 \end{array}$
0.20 wt% HM pectin+0.5wt% gelatine A 0.35 wt.% HM pectin+0.5wt% gelatine A 0.50 wt.% HM pectin+0.5wt% gelatine A		5.75±0.20 10.25±0.34 13.75±0.45

The kinematic viscosity of 0.5 wt.% gelatin type A was significantly higher (at 2.80 mm² s⁻¹) in distilled than in seawater (2.16 mm² s⁻¹) as a result of the denaturing effect of the salt on the gelatin. The denaturing effect of sea water was also confirmed by surface tension measurements. 1 wt.% gelatin type A had a surface tension of 59.9 mN m⁻¹ in distilled water compared to 43.5 mNm⁻¹ in sea water.

Of great interest would be the evaluation of salt concentration on stability. However the focus of this study was the natural concentration in sea water which varies geographically from 33 to 38 gL⁻¹. Similarly, a systematic study of the effect of protein structure on stability and reflectance of foams is desirable particularly if algal blooms were to be considered as the protein source. In the present work, the focus was on materials easily available in commercial quantities. Nevertheless, this study highlights research areas which have been neglected and for which there is considerable scope for exploration.

Conclusions

Here the feasibility of creating foams stabilized by gelation have been investigated using non-toxic biodegradable additives. Such foams last for months in the laboratory environment on still, abiotic seawater. They can have practical applications in food science, in off-shore and marine fire control and they make the prospect for enhancing oceanic albedo feasible.

Foams were stable over the course of the experiment (7.3 Ms:12 weeks) and made use of the electrostatic interactions between positively charged gelatin and negatively charged pectin. They had slow, but nevertheless extensive drainage, which allows sufficient time for electrostatic interactions to develop residual, persistent bright foam in the upper layers. The reflectances were 0.5-0.55 in the visible for 0.35 wt.% and 0.5 wt.% HM pectin-0.5 wt.% gelatin type A foams. These are values characteristic of measurements on oceanic whitecaps.

In contrast, unary solutions of WPI, albumin, and gelatin type A and B showed liquid drainage half life was below 600 s consistent with other research on polydisperse protein foams. Clearly protein additives alone are not suitable.

Foams produced from solutions of iota carrageenan - methylcellulose produced smaller bubbles of around 1 mm diameter with a slightly higher reflectance of 0.65-0.75. Iota carrageenan is derived from seaweed enhancing its environmental acceptability.

^aDepartment of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

^bDepartment of Biochemical Engineering, University College London, Bernard Katz Building, London. WC1E 7JE

Acknowledgments

ARTICLE

The authors are grateful to Linda Bellekom-Allen at Dow Pharma and Food Solutions and to Methe Sonne and Thomas Worm at C.P.Kelco, Denmark. The authors are grateful to Thomas Rowland for experimental assistance.

References

- 1 S.Damodaran, *Journal of Food Science*, 2005, **70**, R54-R66.
- 2 J.M.R.Patino, C.C.Sanchez, M.R.R.Nino, *Advances in Colloid and Interface Science*, 2008, **140**, 95-113.
- 3 E.Dickinson, *Advances in Colloid and Interface Science*, 2011, **165**, 7-13.
- 4 S.A.Magrabi, B.Z.Dlugogorski, G.J.Jameson, *Fire Safety Journal*, 2002 **37**, 21-52.
- 5 H.Mirhosseini, B.T.Amid, *Food Research International*, 2012, **46**, 387-398.
- 6 D. W. Keith, Ann. Rev. Energy Environ., 2000, 25, 245-284.
- 7 J. Shepherd, J. Caldeira, P. Cox, J. Haigh, D. Keith, B. Launder, G. Mace, G. Mackerron, J. Pyle, S. Rayner, C. Redgwell, A. Watson, *Geoengineering the Climate: Science, Governance and Uncertainty, Royal Society Policy Document*, The Royal Society, London 2009 pp. 23-36.
- 8 J.B. Moreno-Cruz, D.W.Keith, *Climatic Change*, 2013, **121**, 431-44.
- 9 A. Costello and 28 others, *The Lancet*, 2009, **373**, 1693-1733.
- 10 G.R. Sullivan, *National security and the threat of climate change*, CNA Corpn. Virginia, USA, 2007.

- 11 J.R.G. Evans, E.P.J. Stride, M.J. Edirisinghe, D.J. Andrews, R. Simons, *Climate Research*, 2010, **42**, 155– 160.
- 12 R. Seitz, *Climatic Change*, 2011, **105**, 365–381.
- 13 C.H. Whitlock, D.S. Bartlett, E.A. Gurganus, *Geophysical Research Letters*, 1982, **9**, 719–722.
- R.E. Payne, Journal of the Atmospheric Sciences, 1972, 29, 959–970.
- 15 R. Seitz, *Earth's Future*, 2013, 1, 45–52, Wiley Online Library doi:0.1002/2013EF000151.
- 16 J.J. Polovina, E.A. Howell, M. Abecassis, *Geophysical Research Letters*, 2008, 35, L03618.
- 17 P. Stevenson, *Foam engineering fundamentals and applications*, Wiley, New Zealand 2012, pp. 8-100.
- 18 P.J. Stabeno, E.C. Monahan, in *Oceanic Whitecaps*, D.Reidel.Publ. Co. 1986, pp.261-266
- 19 Devetzoglou MA, Evans JRG J. Marine Res., (in press)
- 20 Y. Cheng, S-M. Li, A. Leithead, P.C. Brickell, W.R. Leaitch, *Atmos Environ*, 2004, 38, 5789–5800.
- 21 T. Nagata, B. Meon, D.L. Kirchman, *Limnology and Oceanography*, 2003, **48**, 745–754.
- 22 R.J. Pugh, Advances in Colloid and Interface Science, 1996, 64, 67-142.
- 23 P.A. Wierenga, H. Gruppen, Current Opinion in Colloid and Interface Science, 2010, **15**, 365–373.
- 24 M.R. Rodríguez-Niño, C.C. Sánchez, V.P. Ruíz-Henestrosa, J.M.R. Patino, *Food Hydrocolloids* 2005, 19, 417–428.
- 25 A. Saint-Jalmes, M-L. Peugeot, H. Ferraz, D. Langevin, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2005, 263,219–225.
- 26 I. Schmidt, B. Novales, F. Boué, M.A.V. Axelos, Journal of Colloid and Interface Science, 2010, 345, 316–324.
- 27 R. Schrieber, H. Gareis, *Gelatin Handbook Theory and Industrial Practice*. Wiley-VCH, Weinheim 2007 pp. 45-113.
- 28 F.J. Millero, R. Feistel, D.G. Wright, T.J. McDougall, Oceanographic Research Papers 2008, 55, 50–72.
- 29 N. Kitabatake, E. Doi, *Journal of Food Science* 1982, 47, 1218–1221.
- 30 D.J. Carp, R.I. Baeza, G.B. Bartholomai, A.M.R. Pilosof, *Food Science and Technology*, 2004, **37**, 573– 580.
- 31 D.J. Carp, G.B. Bartholomai, A.M.R. Pilosof, *Food Science and Technology*, 1997, **30**, 253 258.
- 32 O.D. Monera, T.J. Sereda, N.E. Zhou, C.M. Kay, R.S. Hodges, *Journal of Peptide Science*, 1995,1, 319–329.
- 33 A. Springsteen, *Analytica Chimica Acta*, 1999, **380**, 183–192.
- 34 F. Grum, G.W. Luckey, *Applied Optics* 1968, 7, 2289–2294.
- 35 X. Qi, C. Holt, D. McNulty, D. Clarke, S. Brownlow, G. Jones, *Biochemical Journal*, 1997, **324**, 341–346.
- 36 A.A. Perez, C.C. Sánchez, J.M. Rodríguez-Patino, A.C. Rubiolo, L.G. Santiago, *Journal of Food Engineering*, 2012, **113**, 53–60.

37 J.I. Loch, A. Polit, P. Bonarek, D. Olszewska, K. Kurpiewska, M. Dziedzicka-Wasylewska, K. Lewiński. *International Journal of Biological Macromolecules*, 2012, 50, 1095–1102.

RSC Advances

- 38 A.A. Townsend, S. Nakai, *Journal of Food Science* 1983, **48**, 588–594.
- 39 K.N. Ryan, B. Vardhanabhuti, D.P. Jaramillo, J.H. van Zanten, J.N. Coupland, E.A. Foegeding, *Food Hydrocolloids* 2012, 27, 411–420.
- 40 H. Zhang, G. Xu, T. Liu, L. Xu, Y. Zhou, Colloids and Surfaces A: Physicochemical and Engineering Aspects 2013, 416, 23–31
- 41 S. Chatterjee, H.B. Bohidar, *International Journal of Biological Macromolecules* 2005, **35**, 81–88.
- 42 C.L. Hinton, Journal of the Science of Food and Agriculture 1950, 1, 300–307.
- 43 G.W.C. Kaye, T.H. Laby, *Tables of Physical and Chemical Constants*, 16th Edn, 1995, Longman, Essex, p 41, 51.
- 44 M. Gobet, M. Mouaddab, N. Cayot, J-M.Bonny, E. Guichard, J-L. Le Quéré, C. Moreau, L. Foucat, *Magnetic Resonance in Chemistry* 2009, 47, 307–312.
- 45 S. Farris, K.M. Schaich, L. Liu, P.H. Cooke, L. Piergiovanni, K.L. Yam, *Food Hydrocolloids* 2011, 25, 61–70.
- 46 M.R.Mangione, D. Giacomazza, D. Bulone, V. Martorana, P.L.S. Biagio, *Biophysical Chemistry* 2003, 104, 95 – 105.
- 47 T. Funami, M. Hiroe, S. Noda, I. Asai, S. Ikeda, K. Nishinari, *Food Hydrocolloids* 2007, 21, 617–629.
- 48 L. Li, P.M. Thangamathesvaran, C.Y. Yue, K.C. Tam, X. Hu, Y.C. Lam, *Langmuir* 2001, **17**, 8062–8068.
- 49 Y. Xu, C. Wang, K.C. Tam, L. Li. *Langmuir* 2004, **20**, 646–652.
- 50 M.H. Sharqawy, J.H. Lienhard, S.M. Zubair, Desalination and Water Treatment 2010, 16, 354–380.



Stable seawater foams with excellent reflectance have been synthesised and characterized. One application of oceanic foams is to increase planetary albedo. 39x30mm (300 x 300 DPI)