Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces B: Biointerfaces 54 (2007) 200–210
COLLOIDS AND SURFACES B
www.elsevier.com/locate/colsurfb

Comparisons of the foaming and interfacial properties of whey protein isolate and egg white proteins

J.P. Davis, E.A. Foegeding *

Department of Food Science, North Carolina State University, Raleigh, NC 27695-7624, United States

Received 10 August 2005; received in revised form 15 September 2006; accepted 16 October 2006
Available online 24 October 2006

Abstract

Whipped foams (10%, w/v protein, pH 7.0) were prepared from commercially available samples of whey protein isolate (WPI) and egg white protein (EWP), and subsequently compared based on yield stress (τ_0), overrun and drainage stability. Adsorption rates and interfacial rheological measurements at a model air/water interface were quantified via pendant drop tensiometry to better understand foaming differences among the ingredients. The highest τ_0 and resistance to drainage were observed for standard EWP, followed by EWP with added 0.1% (w/w) sodium lauryl sulfate, and then WPI. Addition of 25% (w/w) sucrose increased τ_0 and drainage resistance of the EWP-based ingredients, whereas it decreased τ_0 of WPI foams and minimally affected their drainage rates. These differing sugar effects were reflected in the interfacial rheological measurements, as sucrose addition increased the dilatational elasticity for both EWP-based ingredients, while decreasing this parameter for WPI. Previously observed relationships between τ_0 and interfacial rheology did not hold across the protein types; however, these measurements did effectively differentiate foaming behaviors within EWP-based ingredients and within WPI. Interfacial data was also collected for purified β-lactoglobulin (β-lg) and ovalbumin, the primary proteins of WPI and EWP, respectively. The addition of 25% (w/w) sucrose increased the dilatational elasticity for adsorbed layers of β-lg, while minimally affecting the interfacial rheology of adsorbed ovalbumin, in contrast to the response of WPI and EWP ingredients. These experiments underscore the importance of utilizing the same materials for interfacial measurements as used for foaming experiments, if one is to properly infer interfacial information/mechanisms and relate this information to bulk foaming measurements. The effects of protein concentration and measurement time on interfacial rheology were also considered as they relate to bulk foam properties. This data should be of practical assistance to those designing aerated food products, as it has not been previously reported that sucrose addition improves the foaming characteristics of EWP-based ingredients while negatively affecting the foaming behavior of WPI, as these types of protein isolates are common to the food industry.

Keywords: Interfacial rheology; Foam; Yield stress; Whey protein; Dilatational modulus

1. Introduction

Foam is a dispersion of gas bubbles within a liquid or solid continuous phase. This material class is important to the structure and texture of many food products, including various cakes, confections, meringues, etc. [1]. Two common and important ingredients often found in these products are proteins and sugars. With regards to the foam properties, proteins function as surfactants by adsorbing at the freshly created air/water interface during bubble formation [2]. This adsorption lowers the interfacial tension, which promotes bubble formation. Immediately after and during the initial adsorption, protein–protein attractions at the interface can result in network formation, which promotes bubble stability [3]. Besides their obvious contribution to product flavor, sugars also contribute to the functional properties of foam. For example, sugars are known to improve the stability of foams to gravity induced drainage, primarily by their capacity to increase solution viscosity [4,5]. Furthermore, studies at model interfaces also suggest that sugars affect the interfacial behavior of proteins by exerting an influence on their structure [6–9].

There are various means of assessing the foaming performance of proteins, including their capacity to form (foamability), stabilize and impart specific foam rheological properties.

* Corresponding author at: North Carolina State University, Department of Food Science, Box 7624, Raleigh, NC 27695-7624, United States. Tel.: +1 919 513 2244; fax: +1 919 515 7124.
E-mail address: allen_foegeding@ncsu.edu (E.A. Foegeding).

0927-7765/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfb.2006.10.017

Controlling and predicting foam rheology is especially important when considering the final structural stability and texture of foamed food products. The most important physical factor governing foam rheology is air phase fraction (ϕ) of the foam. Foams transition from viscous fluids to semi-solid-like structures as ϕ increases from zero above the random close pack volume, $\phi_{rcp} \approx 0.64$ [10]. Above ϕ_{rcp}, the formerly spherical bubbles begin contacting one another, forming so called "polyhedral" or "dry" foams. There is an ever developing quantitative framework to describe the unique rheological behaviors of polyhedral foams and concentrated emulsions, as the two systems share many similarities [3,10].

Polyhedral foams display a yield stress (τ_0), which is a solid-like behavior that can be effectively measured via vane rheometry [11]. Previous work established that it takes less protein and less whipping time for standard egg white protein (std-EWP) to produce foams with significantly higher τ_0 as compared to whey protein isolate (WPI) [12]. It has been generally concluded that differences in ϕ or equilibrium surface tension (γ) for the two protein types do not adequately explain differences in τ_0 for the two protein ingredients [12,13], despite the fact that γ and ϕ are prominent within theoretical equations applied to the rheology of such colloidal systems (polyhedral foams and concentrated emulsions) [10,14,15]. Others have experimentally verified that the shear elastic modulus (G') relates to ϕ for both concentrated emulsions [10,16] and whipped foams prepared from EWP solubilized in high contents of invert sugar [17]. As discussed by Dimitrova and Leal-Calderon, most models pertaining to polyhedral foam or concentrated emulsion rheology implicitly assume constant interfacial tension during perturbation [18]. While this may be a valid assumption for the rapid interfacial relaxations of small molecular weight surfactants (SMWS) under interfacial perturbations, this is likely not to be the case for adsorbed proteins layers. Accordingly, there is a limited amount of theoretical work suggesting the interfacial rheological properties of a surfactant significantly influence bulk foam or emulsion rheology [19,20]. Experimental evidence for such phenomena is also beginning to emerge. For example, data for protein-stabilized, concentrated emulsions revealed a positive correlation between the dimensionless bulk elasticity, $G'/(\gamma/r)$ of the emulsions and the interfacial dilatational elasticity (E') of the stabilizing proteins, where r is equal to the radius of the dispersed phase [18]. In our own lab, recent work with whey proteins suggest a link between the dilatational rheological properties of the air/water interface and foam τ_0. Specifically, proteins and/or peptides which induce high values of E' and/or a low viscous modulus at a model air/water interface seem to promote high values of τ_0 when used to produce foams [21–23]. However, comparison of these interfacial and foaming measurements have not been extended to whipped foams prepared from other proteins, specifically EWP, which is the traditional foaming agent of choice in the food industry.

There is a relative abundance of data pertaining to the interfacial behaviors of β-lactoglobulin (β-lg) and ovalbumin, the two primary proteins in WPI and EWP, respectively, with several recent examples being cited here [24–28]. While these analyses have improved our understanding of how isolated proteins behave at model phase boundaries, isolated proteins are rarely, if ever, used to make foams in the food industry. Furthermore, there seems to be a lack of studies that directly measure both interfacial and foaming properties of the same material, especially foaming studies that utilize a protein concentration relevant to the food industry, i.e. ≥5% (w/v) protein, and utilizes whipping as a means of bubble production, again the most industrially relevant method of foam formation. Accordingly, we choose to whip foams from 10% (w/v) protein solutions utilizing commercially available samples of WPI and EWP followed by interfacial measurements with the same solutions (or their dilutions).

The overall goal of the current work was to determine the interfacial dilatational rheological basis, if any, behind the different foaming properties of EWP and WPI. In conjunction with this goal, the effects of high sucrose concentrations on the foaming and interfacial behavior of EWP and WPI were assessed, as sucrose is a common co-solute in protein-based aerated food products. Work with model interfacial systems generally suggests the adsorption rates of globular proteins are suppressed at interfacial boundaries in the presence of sugars [7,8,29], although there is also evidence that sucrose addition may increase globular protein adsorption [6]. Interfacial rheological data of proteins in the presence of sugars is much more limited. The interfacial dilatational viscoelasticity of bovine serum albumin (BSA) was found to decrease when co-solubilized with 1 M sucrose [30]. Clearly, more data is needed to better understand sugar/protein interactions both at the interface and in foaming systems, due to the practical interest of those preparing aerated food products containing protein and sweeteners.

2. Materials

A commercial sample of WPI (BiPro, 94% protein, dry basis) was supplied by Davisco Foods International, Inc. (Le Sueur, MN). Two types of spray dried egg white protein (82% protein, dry basis) were obtained from Primera Foods (Cameron, WI): (1) standard egg white protein and (2) high whip egg white protein (hw-EWP). These products are essentially identical except the hw-EWP had not more than 0.1% sodium lauryl sulfate added as a whipping agent by the manufacturer. High purity β-lactoglobulin (approximately 90%; product # L3908), ovalbumin (Grade V, minimum 98%; product # A5503) and sucrose (SigmaUltra, ≥99.5%; product # S7903) were purchased from Sigma Chemicals Co. (St. Louis, MO). All other chemicals were of reagent grade quality. Deionized water was obtained using a Dracor Water Systems (Durham, NC) purification system. The resistivity was a minimum of 18.2 MΩ cm.

3. Methods

3.1. Hydration

Samples were initially hydrated to 10% (w/v) protein. Prior to the final volume adjustment, the pH of all solutions was adjusted to 7.0. Solution pH is well established to affect both foaming and interfacial properties of proteins [23,28,31,32]. The current

preparations were adjusted to pH 7.0 as many aerated commercial food products are prepared at or near this pH. When required, sucrose was added to the protein solutions on a % w/w basis.

3.2. Foam generation

A Kitchen Aid Ultra Power Mixer (Kitchen Aid, St. Joseph's, MI) with a 4.5 qt (4.3 L) stationary bowl and rotating beaters was used for foam formation. 10% (w/v) protein solutions (225 mL) were whipped at speed setting 8 (planetary rpm of 225 and beater rpm of 737), 20 min for WPI solutions and 15 min for EWP solutions, both in the presence and absence of 25% (w/w) sucrose. As mentioned earlier, it is established to take less whipping time to produce foams with equivalent yield stress from std-EWP as compared to WPI. The 15 min whip time for the EWP solutions was utilized to prevent overbeating.

3.3. Yield stress measurements

Foam yield stress was determined by vane rheometry [11]. A Brookfield 25xLVTDV-ICP (Brookfield Engineering Laboratories, Inc. Middleboro, MA) viscometer was used at a speed of 0.3 rpm. The vane had a 10 mm diameter and 40 mm length. Maximum torque response (M_0) was documented for each of three measurements taken per foam and used to calculate yield stress according to published information [33,34]:

$$\tau_0 = \frac{M_0}{[(h/d) + (1/6)]((\pi d^3)/2)} \quad (1)$$

where τ_0 is the yield stress, and h and d are the height and diameter of the vane. Three consecutive measurements (4 min maximum) were taken per foam, and each solution type was replicated a minimum of three times.

3.4. Overrun

Overrun measurements were begun immediately after the final τ_0 measurement. Foam was carefully scooped from the bowl in a circular pattern with a rubber spatula, filling a standard weigh boat (100 mL) three times. The mean value was used to calculate overrun and air phase fraction according to [1]:

$$\%\text{Overrun} = \frac{(\text{wt. 100 mL solution}) - (\text{wt. 100 mL foam})}{\text{wt. 100 mL foam}} \times 100 \quad (2)$$

$$\text{Air phase fraction}(\phi) = \frac{\%\text{overrun}}{(\%\text{overrun} + 100)} \quad (3)$$

Overrun measurements were stable over the measurement time (3 min maximum). Each treatment was replicated a minimum of three times to determine the average overrun.

3.5. Stability measurements

Foam drainage was measured based on the method of Phillips et al. [35]. Drainage measurements were begun immediately after the final overrun measurement. The time for half of the pre-foam mass to drain through a hole in a whipping bowl was taken as a measurement of foam stability. Note that the mass of foam removed during the overrun measurements was subtracted when calculating half of the pre-foam mass. The starting time for these measurements was taken as immediately after foam formation.

3.6. Interfacial measurements

The foaming solutions or their dilutions were used for interfacial measurements. Pendant drop tensiometry is an established method for measuring surfactant behavior at liquid phase boundaries [36,37]. An automated contact angle goniometer (Rame-Hart Inc., Mountain Lakes, NJ) was used for data collection and calculations in combination with the DROPimage computer program [38]. Measurements were made from vertical drops (16 μL) dangling from a capillary into an environmental chamber with standing water at its bottom to minimize evaporation, and all measurements were made at room temperature ($23 \pm 1\,^{\circ}\text{C}$). When required, changes in γ were monitored with a 1-s resolution. Sinusoidal oscillations of the drops' areas were input by a volume amplitude of 0.5 μL, and the resulting change in γ was used to determine the dilatational modulus. From the modulus and from the phase angle between the surface area change and surface tension response, the DROPimage software calculates E' and E'', which are equivalent to and proportional to the elastic and viscous components of the interface, respectively. The details for these calculations have been described elsewhere [38]. Frequencies applied in this work ranged from 0.04 to 0.1 Hz. Preliminary work confirmed this strain amplitude was within the linear viscoelastic regime for all samples at all frequencies and corresponded to a relative interfacial area change of ~2.3%.

3.7. Density determination

Densities of the component phases are required inputs for the determination of interfacial tension from the shape analysis of drops and bubbles [39]. Accordingly, a Mettler-Toledo DE40 density meter (Mettler-Toledo, Columbus, OH) equipped with a viscosity correction card was used to determine the density of each solution at 23 °C. The accuracy of the instrument was 1×10^{-4} g/cm^3 and every solution was measured in duplicate and averaged prior to interfacial measurements.

4. Results and discussion

The foaming properties of the different protein solutions (10%, w/v, pH 7.0), both in the presence and absence of 25% (w/w) sucrose, are summarized in Fig. 1. Foam yield stress (τ_0) was significantly greater for both the standard egg white protein and the high whip egg white protein as compared to WPI (Fig. 1A). This is in agreement with previously reported data for WPI and std-EWP [11–13]. Overrun was slightly higher for WPI than either std-EWP or hw-EWP in the absence of 25% (w/w) sucrose (Fig. 1B). Sugar addition significantly decreased

overrun for all three foaming ingredients (Fig. 1B), in agreement with earlier work [40]. The time required for half of the pre-foam mass to drain through a hole near the base of the whipping bowls was taken as a measurement of foam stability [22,35]. As seen in Fig. 1C, half life was significantly greater for the std-EWP and hw-EWP foams as compared to WPI, both in the presence and absence of 25% (w/w) sucrose. Sucrose addition significantly increased foam half life for the std-EWP and hw-EWP foams, whereas sucrose addition minimally affected the drainage rates of the WPI foams (Fig. 1C). Previous work found the addition of 10% sucrose decreased foam overrun and increased the stability against drainage of whipped WPI solutions and improved foam stability against drainage [40].

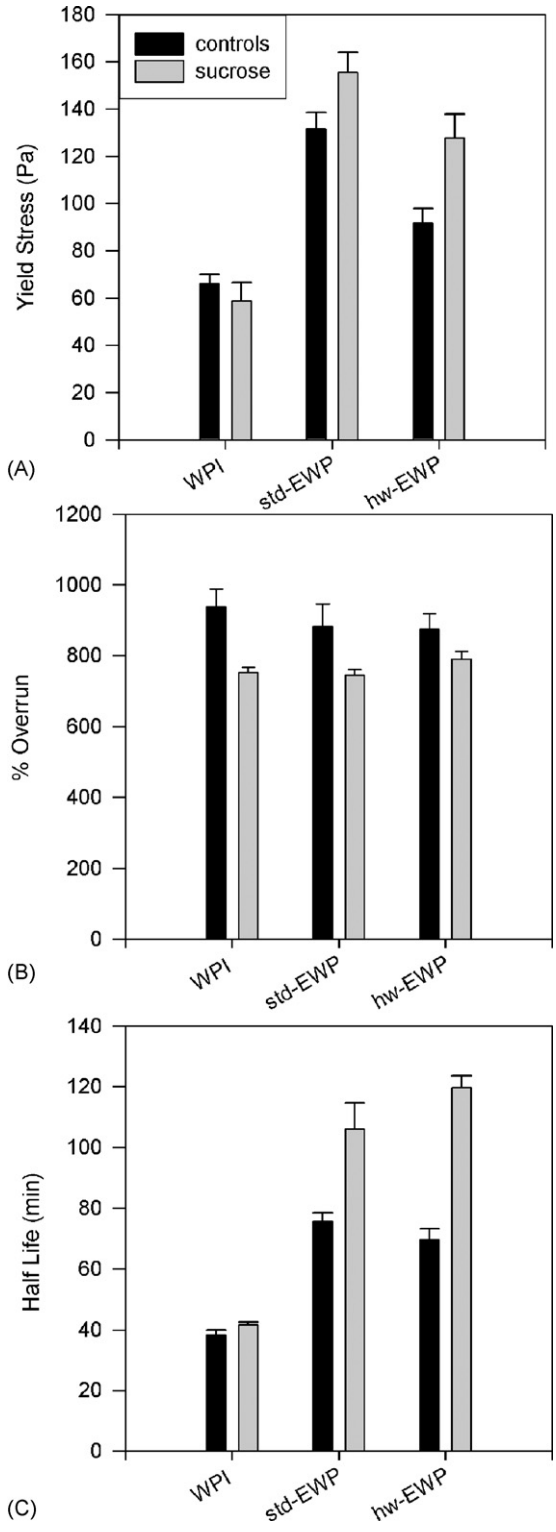

Fig. 1. Yield stress (A), overrun (B) and half-life (C) data of foams prepared from various 10% (w/v) protein solutions at pH 7.0, both in the presence and absence of 25% (w/w) sucrose. Error bars are standard deviations of mean values. Symbols appear on the figure.

Foam yield stress (τ_0), like all foam rheological measurements, strongly depends on the amount of air incorporated into the continuous phase or its air phase volume (ϕ). Application of Eq. (3) to the overrun measurements presented in Fig. 1B revealed all foams had $\phi \geq 0.88$, well above ϕ_{rcp}, meaning they can be considered polyhedral. Equations describing polyhedral foam rheology predict τ_0 to increase with increasing ϕ and/or decreasing bubble size [14,15]. A simple comparison of Fig. 1A and B reveals that τ_0 and overrun, which is directly proportional to ϕ as seen in Eq. (3), do not positively correlate in the current foams. However, such conclusions are limited without an accurate description of the bubble size distribution. Confocal microscopy is one technique applied to characterizing bubble sizes in foams [12,17]. Direct comparison of 10% (w/v) protein foams of WPI and std-EWP, each solubilized in the presence of approximately 16.2% (w/v) powdered sugar, revealed no difference in bubble size distribution [12]; however, this may reflect a limitation of the method and not an actual physical phenomenon. Lau and Dickinson observed qualitative differences in bubble size over whipping time with EWP solubilized in a high content of invert sugar; however, the phase volumes of these foams were significantly lower ($\phi \leq \sim 0.54$) [17].

Comparison of τ_0 and drainage stability (Fig. 1A and C) revealed a positive correlation between the two measurements. Increases in τ_0 with increasing foam stability is logical, as more stable foams should have higher ϕs and smaller bubbles, both of which should increase τ_0 [14]. Interestingly, addition of 25% (w/w) sucrose significantly improved the two EWP-based ingredients resistance to drainage, whereas for WPI, sucrose addition minimally affected drainage rates (Fig. 1C). If the increased resistance to drainage was solely attributable to an increase in continuous phase viscosity [4,5], one might expect a uniform retardation in drainage for all three foaming ingredients. Since this was not observed, it seems sucrose addition affected the structural/functional properties of the various proteins differently, as discussed later.

Adsorption rates at the air/water interface of the three foaming solutions were measured by qualitatively assessing the rate of γ decline for freshly formed pendant drops [41–43]. Data for 10% (w/v) protein solutions are presented in Fig. 2. Adsorption rates were most rapid for the hw-EWP solution, followed by std-EWP and then WPI, both in the presence and absence of 25% (w/w) sucrose. As mentioned previously, the hw-EWP ingredient contained, approximately, 0.1% sodium lauryl sulfate, in addition to the albumin protein also found in the std-EWP. Sodium lauryl sulfate is a typical SMWS, which are characteristically more effective than proteins at rapidly decreasing γ [44]. Furthermore, work with protein/SMWS mixtures have shown

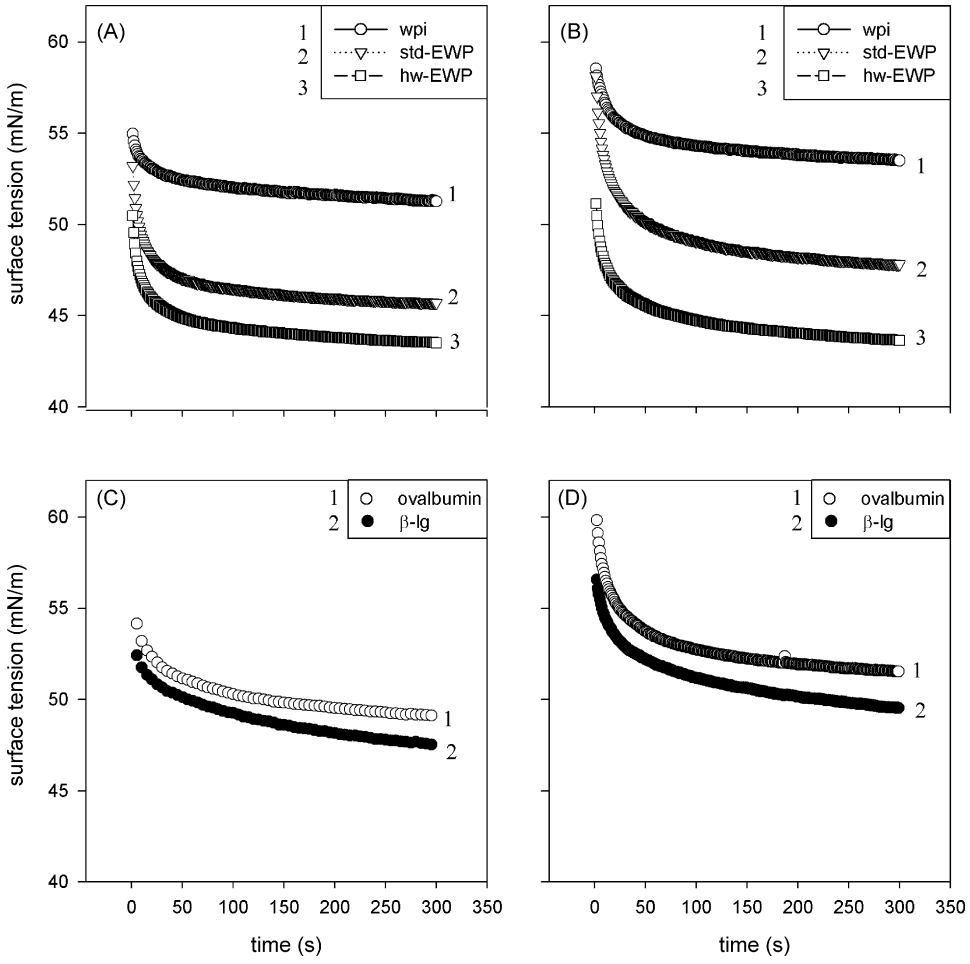

Fig. 2. Typical dynamic surface tension measurements of 10% (w/v) protein solutions. A and C: Protein solutions only; B and D: protein solutions made to 25% (w/w) sucrose. Symbols appear on the figure.

that small amounts of SMWS, relative to protein, can profoundly increase the rate of γ decline relative to that observed for proteins in the absence of SMWS [44]. Therefore, the presence of sodium lauryl sulfate in the hw-EWP ingredient likely explains its more rapid decrease in γ as compared to WPI and std-EWP, which contained only protein as surfactants.

To better understand adsorption behavior of the commercial protein isolates, the dynamic surface tension response for 10% (w/v) solutions of purified β-lg and ovalbumin, which are the predominant proteins in WPI and EWP, respectively, are also presented in Fig. 2. Adsorption rates for these two proteins were similar both in the absence (Fig. 2C) and presence of 25% (w/w) sucrose (Fig. 2D), and the presence of sucrose retarded the rate of surface tension decline for these two proteins. It is notable that the rate of γ decline was similar for β-lg and ovalbumin (Fig. 2C or D), as compared to WPI and std-EWP for which γ decline was different, with std-EWP adsorbing much more rapidly (Fig. 2A or B). This suggests other proteins present in the commercial preparations and/or differences in their processing histories are affecting adsorption rates.

Sucrose addition retarded the rate of γ decline for WPI, std-WPI, β-lg and ovalbumin, while minimally affecting the adsorption of hw-EWP (Fig. 2). Conflicting reports exist in the literature as to the effects of added sucrose on protein adsorption. For example, bovine serum albumin was found to adsorb more rapidly at the air/water interface in the presence of 1 M (∼34%, w/v) sucrose during the first stage of adsorption, in which diffusion dominates this process [6]. A potential explanation was that the protein molecule would be more compact in sugar solutions, due to the well established phenomenon of preferential hydration [45], and hence adsorb more rapidly. It was also noted that the increased solution viscosity imparted by the sugar solutions should limit diffusion to the interface, meaning protein adsorption in sugar solutions should be a balance of these two phenomena. In a separate study, increasing concentrations of sucrose, up to 40% (w/w) (∼1.4 M), were found to decrease the adsorption rate of BSA [7]. Potential explanations included the increased solution viscosity, the potential for direct sucrose–protein interactions with which would decrease the molecule's hydrophobicity and preferential hydration of the proteins. Ovalbumin was also found to adsorb less rapidly at the air/water interface in the presence of sucrose [29], in agreement with the current data. Mixing calorimetry data suggested ovalbumin participated in hydrogen bonding with the sucrose molecule, potentially decreasing its hydrophobicity and hence its surface activity.

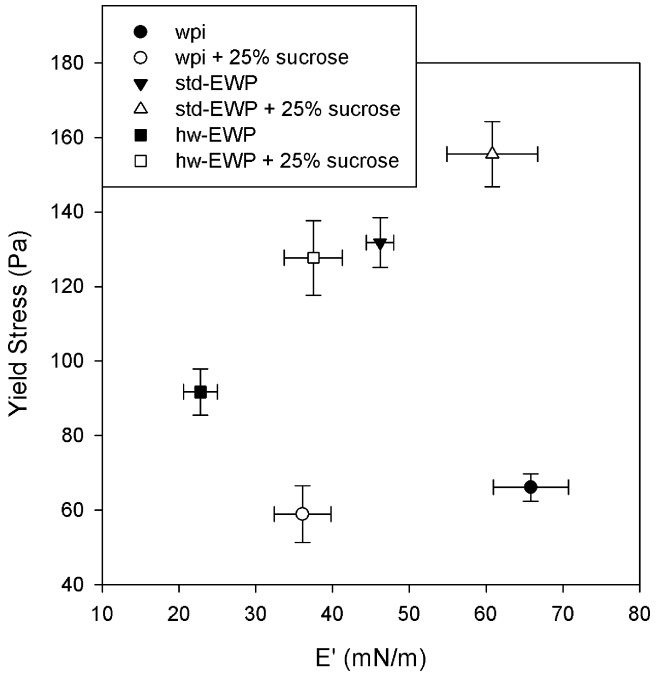

Fig. 3. Interfacial dilatational elasticity vs. yield stress of various protein solutions, both in the presence and absence of 25% (w/w) sucrose. All measurements were made at a protein concentration of 10% (w/v). Frequency of oscillation for interfacial measurements was 0.04 Hz and samples were aged 5 min. Values shown are averages of at least three independent replications and error bars are the standard deviations.

It is noted that in the above cited adsorption studies, the protein concentrations were all several orders of magnitude more dilute than concentrations (5–10%, w/v) typically found in industrial food foams. In the current work, it was decided to primarily focus on adsorption rates for 10% (w/v) protein solutions as it may more closely mimic actual food foams. Specifically, the degree of interfacial protein unfolding, which contributes to decreases in γ, may be overemphasized for adsorption studies utilizing very dilute solutions, as interfacial protein unfolding is well documented to increase upon dilution [46]. Potential reasons for adsorption retardation in the presence of sucrose have already been discussed. If sucrose addition was restricting surfactant adsorption primarily via an increase in solution viscosity, it could be hypothesized all surfactants would show proportional decreases in γ decline, which does not seem to be the case. However, if sucrose is affecting the structure of the surfactant molecules, these effects should be minimal for the sodium lauryl sulfate present in the hw-EWP, due to its simpler structure as compared to proteins, potentially explaining the lessened effect sucrose addition had on hw-EWP adsorption.

As seen in Fig. 1, the addition of 25% (w/w) sucrose to each protein solution decreased foam overrun. It is established that overrun measurements can be influenced by drainage rates, that is, decreased liquid drainage increases foam density and hence decreases overrun, while increased liquid drainage decreases foam density, making overrun measurements higher [4]. We have suspected this phenomena in earlier work [22] and it cannot be ruled out with the current foaming solutions. An alternative explanation for the drop in overrun upon adding 25% (w/w) sucrose is the reduced adsorbance observed in these foaming solutions upon equivalent sucrose addition (Fig. 2). This is because the capacity of a surfactant to rapidly decrease γ promotes bubble formation and hence increase ϕ [47]. However, the HW-EWP was most effective at lowering γ in the current solutions, yet overrun of these foams was actually the lowest observed.

Previous work with whey protein: (1) solubilized across a range of electrostatic conditions [23], (2) in the presence of various amounts of polymerized whey protein [22] and (3) after hydrolysis with various enzymes [21], revealed potential relationships between interfacial rheology and foam rheology. Specifically, proteins and/or peptides which induce high values of E' and/or a low viscous modulus at a model air/water interface seem to promote high values of τ_0 when used to produce foams. E' is the amount of recoverable energy upon dilatational interfacial deformations and can be thought of as the stiffness of a surfactant covered interface to dilatational motions [48]. The phase angle is proportional to ratio of the viscous modulus (energy lost upon dilatational interfacial deformations) and elastic modulus, with higher phase angles indicative of a

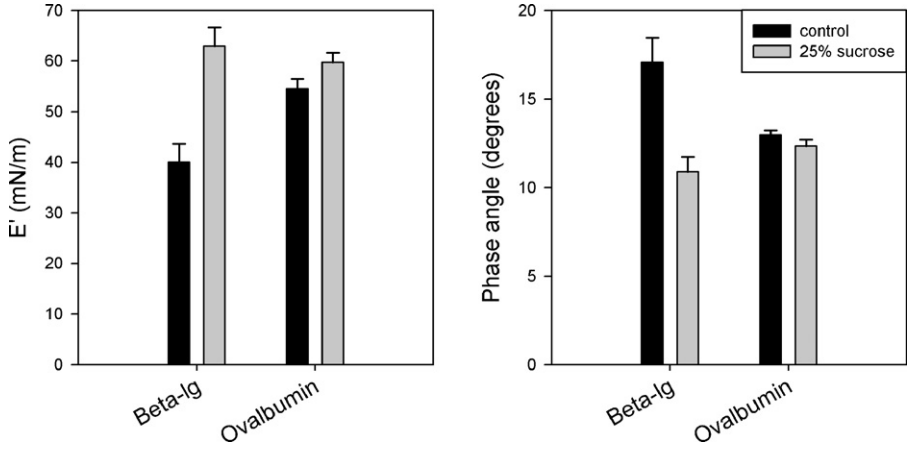

Fig. 4. Interfacial dilatational elasticity of adsorbed β-lactoglobulin and ovalbumin, both in the presence and absence of 25% (w/w) sucrose. All measurements were made at a protein concentration of 10% (w/v). Frequency of oscillation for interfacial measurements was 0.04 Hz and samples were aged 5 min. Values shown are averages of at least three independent replications and error bars are the standard deviations.

proportional increase in the viscous modulus [48]. For the above mentioned studies [21–23], interfacial dilatational rheological properties of the various solutions were analyzed via an oscillating pendant drop. Conditions were specific, and included a 16 μL capillary drop which had been aged 5 min, prior to oscillation at 0.04 Hz with either a 1 or 0.5 μL amplitude, corresponding to, approximately, 5 and 2.3% area changes, respectively. Note that the amplitude was reduced for several of the highly elastic β-lg hydrolysates to ensure a linear viscoelastic response [21]. The same interfacial test (0.5 μL amplitude) was applied to the current solutions, both in the presence and absence of 25% (w/w) sucrose, and the resulting E' values are plotted with τ_0 in Fig. 3. The protein concentration for the interfacial measurements was 10% (w/v), identical to that actually used in the foaming measurements. It is clearly seen in Fig. 3, that EWP-based foams have significantly higher values of τ_0, despite lower and/or equivalent values of E' at a model air/water interface. Striking also were the differing effects addition of 25% (w/w) sucrose had on the foaming ingredients, as sucrose addition increased E' for EWP-based ingredients, whereas sucrose addition decreased this parameter for WPI (Fig. 3).

Oscillations at 0.04 Hz were also conducted for the pure solutions (10%, w/v) of β-lg and ovalbumin to understand how these proteins responded to the addition of sucrose (Fig. 4). In contrast to WPI, the addition of 25% (w/w) sucrose increased the elasticity and decreased the phase angle of adsorbed β-lg interfaces, while sucrose addition minimally affected the rheology of adsorbed ovalbumin interfaces (Fig. 4). Reasons for these differences could be attributed to numerous factors, which again include different processing histories and/or compositions; however, regardless of the cause for these differences, this data clearly underscores the importance of inferring interfacial mechanisms from the same materials which are being utilized in the bulk property of interest (foams in this case).

To further explore the interfacial rheological behaviors of these various foaming ingredients, it was decided to increase the frequency of oscillation to 0.1 Hz for several reasons, which included: (1) the perturbations actual foams experience during their formation and subsequent processing are likely much more rapid than even 0.1 Hz, which is approaching the upper frequency limit of the instrument, (2) the limiting interfacial dilatational elasticity (E_0) of proteins should be approached under a given set of conditions as the frequency of oscillation is increased [49] and (3) increases in frequency allows for more information to be collected within a given measurement time.

Data for WPI, std-EWP and hw-EWP, all in the absence of sucrose, are presented in Fig. 5, where the first measurable data point of E' is plotted as a function of surface pressure (Π). Note that $\Pi = \gamma_0 - \gamma$, where γ_0 is the surface tension of the solvent (water in this case), and γ is the surface tension of the solution at a given time. Both the foaming samples and their dilutions were analyzed, with the goal of dilution being to better understand the effect of bulk protein concentration of interfacial rheology. The frequency of oscillation was 0.1 Hz and was begun immediately after drop formation. Each measurement was the average of 5 periods, and was hence 50 s long. As the first measurement was thrown out for all samples to allow for a minimal equilibrium, the measurements in Fig. 5 were made between 50 and 100 s for all solutions except for those of maximal dilution (0.013%, w/v), for which there was typically a time lag prior to elasticity detection. This is because a minimal adsorbed amount (Γ) is necessary to induce an interfacial rheological response, and for the maximally diluted samples, this minimal adsorption took longer to reach due to diffusion considerations [49].

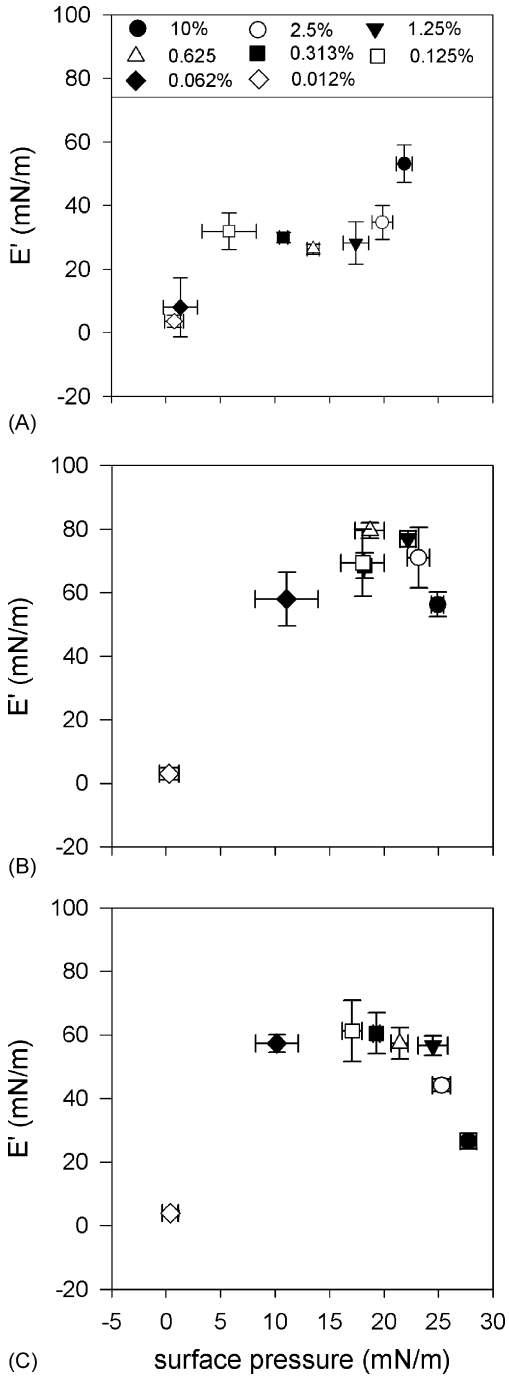

Fig. 5. First measurable data point of interfacial dilatational elasticity vs. surface pressure for various proteins in the absence of sugar. Symbols for protein concentrations appear on the graph. Frequency of oscillation was 0.1 Hz. (A) WPI, (B) std-EWP, (C) hw-EWP. Points are the average of at least three independent replications and error bars are standard deviations.

It is noted that Π decreased for all solutions upon increased dilution of the foaming agents (Fig. 5). This was expected, as the capacity of a surfactant to decrease γ, and hence increase Π, is closely related to its bulk concentration, primarily due to diffusion considerations [49]. As seen in Fig. 5, E' of WPI displayed a sigmoidal response with increasing concentration/Π, with E' ultimately peaking at 10% (w/v) protein. In contrast, E' of the std-EWP and hw-EWP solutions peaked at lower concentrations/Πs than WPI, with peak values occurring near 0.625% (w/v) protein for std-EWP, and between 0.063 and 1.25% (w/v) protein for the hw-EWP.

As discussed by Lucassen-Reynders, the capacity of a surfactant to stabilize interfaces does depend on E'; however, it is not a simple proportionality [50]. Instead, foaming agents are most effective at concentrations such that E' increases as the bulk concentration of surfactant decreases. This is because during the dynamics of foam formation and breakdown, surfactant is constantly being depleted, either by expansion of the interfaces, or through losses due to drainage [50]. As seen in Fig. 5, this condition is fulfilled with the two EWP-based ingredients, but not for WPI. The peak in E' followed by a gradual decline with increasing concentration is expected for all SMWSs, as this effect is not necessarily a function of any interfacial intermolecular interactions, which are minimal for this class of surfactants. Instead, it results from increasing bulk surfactant concentrations leveling off the gradients in interfacial tension which are manifest in E' [50]. This likely explains the response of hw-EWP as a function of concentration, since it contained approximately 0.1% sodium lauryl sulfate as an additional whipping agent.

Interfacial measurements were extended to longer times to observe aging effects on the dilatational rheology of the various foaming solutions and their dilutions. Data for WPI, std-EWP and hw-EWP, all in the absence of sucrose, are presented in Fig. 6, where both E' and the phase angle of the various solutions are plotted against Π. The non-diluted solutions (10%, w/v protein) and maximally diluted samples (0.013%, w/v protein) were each analyzed for ~1 h, whereas the other samples were typically analyzed for approximately 20 min. The frequency of oscillation was 0.1 Hz and was begun immediately after drop formation. The slope of E' versus Π for WPI increased as the bulk protein concentration was increased (Fig. 6), which is in general agreement with similar data for WPI [51] and theoretical equations for protein adsorption/interfacial rheology [2]. A maximum in E' was observed for WPI at the highest protein concentration tested (10%, w/v), prior to a slight decrease in this parameter upon increased aging. Analysis of the phase angles for WPI as a function of Π suggested a transitional behavior between approximately 0.625 and 1.25% (w/v) protein (Fig. 6). At concentrations $\geq$ 1.25%, the phase angle decreased sharply with increasing Π, meaning the interfacial layer was becoming more elastic and less viscous with time. At concentrations up to approximately 0.625%, the phase angle was essentially increasing, as a minimal interfacial concentration was building, prior to the point were the interface starts becoming more elastic.

The interfacial rheological behavior of the std-EWP and hw-EWP ingredients displayed several notable differences as compared to WPI (Fig. 6). The slope of E' versus Π did increase with increasing concentration/Π for both EWP-based ingredients, but not as drastically as observed for WPI (Fig. 6). Also, E' of undiluted std-EWP and hw-EWP solutions showed no decline over the 1 h test period, whereas WPI did display a maximum in E' followed by a slight decrease (Fig. 6). Transitions in which

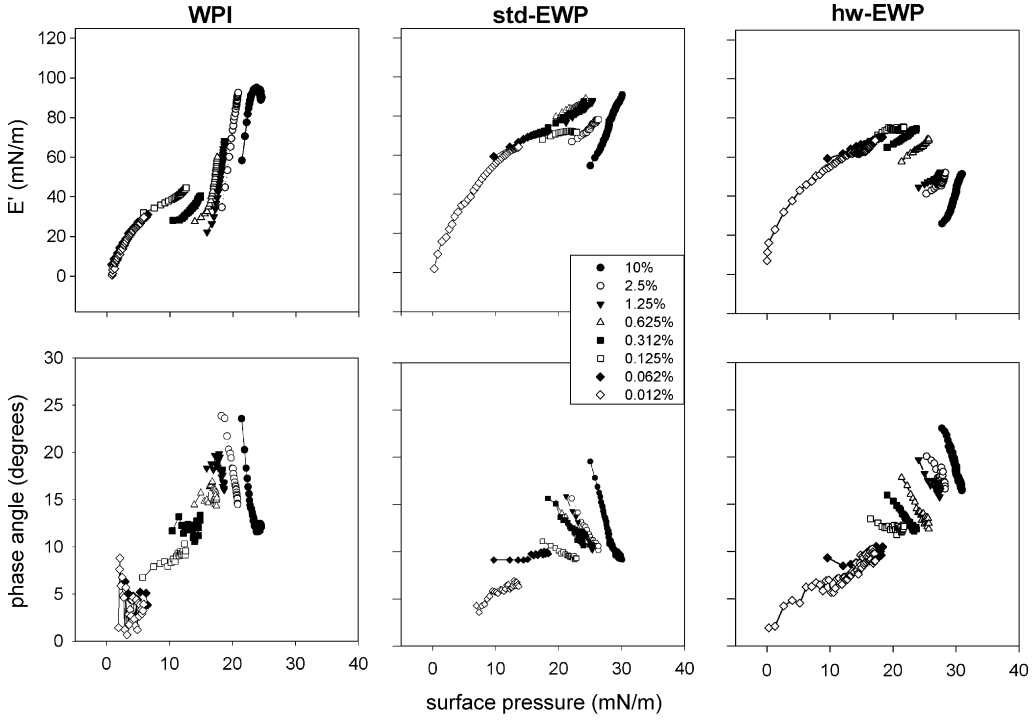

Fig. 6. Interfacial dilatational elasticity and phase angle vs. surface pressure for various proteins in the absence of sucrose. Symbols for protein concentrations appear on the graph. Frequency of oscillation was 0.1 Hz. Values shown are representative of typical observations.

the phase angle began to decrease with age were also observed for both the std-EWP and hw-EWP; however, these transitions occurred at lower concentrations, somewhere between 0.125 and 0.312% for both EWP-based ingredients (Fig. 6).

Surface equation of states developed for SMWSs are inadequate to describe the complex adsorption behaviors of proteins [2]. All protein adsorption studies are characterized by extreme non-ideal behavior such that Π is not proportional to the surface concentration (Γ) even at very low surface pressures [2]. This non-ideal thermodynamic behavior ultimately results from both reorientations of proteins and protein–protein interactions at the interface [49]. In plots of E' versus Π, this non-ideal behavior is manifest in the steep slopes often observed for various types of proteins [2,49]. Analysis for the current protein ingredients reveals that WPI shows extreme non-ideal behavior at much lower concentrations than either EWP-based ingredient. That is, a rapid increase in the slope of E' versus Π is observed at surface pressures above approximately 15 mN/m, with values typically ranging between $\Delta E'/\Delta\Pi = 15$–16 (Fig. 6). Patino and others applied such an approach to WPI adsorbed at the oil/water interface using pendant drop tensiometry (0.1 Hz, 15% area amplitude, pH 5.0, $I = 0.05$ M) [51]. These authors reported a rapid increase in the slope of E' versus Π, at surface pressures above approximately 12.5 mN/m, which generally agrees with the current data for WPI at the air/water interface. However, the slope of E' versus Π was considerably less steep (approximately 4) for WPI adsorbed at the oil/water interface, which may reflect either a difference in the two types of interfaces or a pH effect.

In contrast to WPI, the slopes of E' versus Π for the std-EWP did not intensify as rapidly upon increasing protein concentration (Fig. 6). This suggests the adsorbed form of the std-EWP proteins is more consistent across the concentration regimes of adsorption. Similarly, the hw-EWP ingredient also displayed less non-ideality in its plot of E' versus Π, as only at the highest concentration tested, did the slope of E' versus Π become noticeably steeper.

It is clear from Figs. 5 and 6, that the concentration of protein (or SMWS) strongly influences the interfacial rheological response of such materials. With the primary goal of interfacial measurements being the replication of conditions actually found in protein-based foams, it was decided to investigate the effects of added sucrose on foaming ingredient interfacial rheology at a protein concentration of 10% (w/v). This data is summarized in Fig. 7. The frequency of oscillation was 0.1 Hz and all samples were tested for 20 min. Note that in calculating Π for the sucrose containing solutions, values of ~74.4 and 77.0 mN/m were used for γ_0, as these were experimentally determined for 25 and 50% (w/w) sucrose solutions in water, respectively, in general agreement with previously reported data concerning sucrose solutions [52]. Increasing concentrations of sucrose decreased E' for WPI in addition to lowering the phase angle of this material, while imparting exactly opposite effects for the EWP-based ingredients (Fig. 7). Earlier work with BSA did find sucrose addition (1 M) to decrease the interfacial viscoelasticity of this molecule [30]. The reasons for these contrasting effects for WPI and EWP are not clear; however, this does seem to reflect in the foam properties, including τ_0 and drainage rates. The slope of E' versus Π was decreased for all samples upon sucrose addition; however, this was more apparent for the two EWP-based ingredients (Fig. 7).

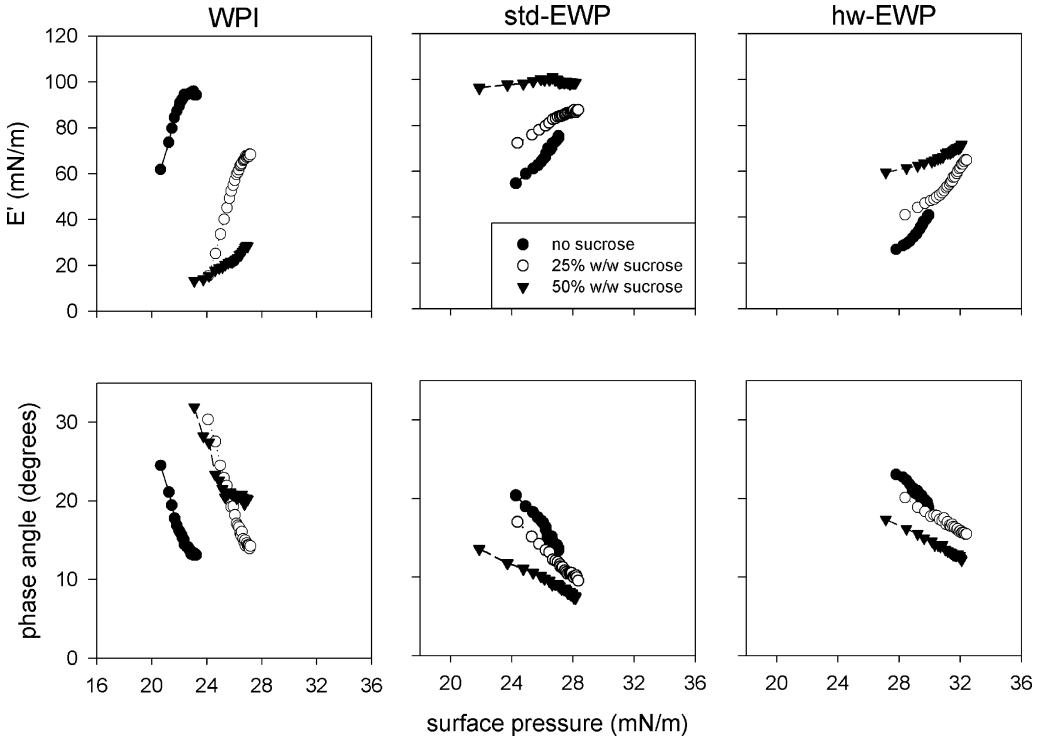

Fig. 7. Interfacial dilatational elasticity and phase angle vs. surface pressure for 10% (w/v) protein solutions as affected by sucrose. Symbols for sucrose concentrations appear on the graph. Frequency of oscillation was 0.1 Hz. Values shown are representative of typical observations.

5. Conclusions

Interfacial tests at a model air/water interface were utilized to investigate differences in foaming behaviors between WPI, std-EWP and hw-EWP. Adsorption rates at the air/water interface were most rapid for hw-EWP, followed by std-EWP and then WPI. The rapid adsorption of hw-EWP was attributable to the additional 0.1% (w/w) sodium lauryl sulfate added to this ingredient. Addition of 25% (w/w) sucrose slowed the rate of surface tension decline for WPI and std-EWP, but minimally affected adsorption of the hw-EWP. Addition of 25% (w/w) sucrose significantly increased τ_0 and drainage resistance of the EWP-based foams; however, equivalent additions of sucrose to WPI resulted in reduced τ_0 and essentially similar drainage rates. Interfacial rheological tests revealed sucrose to be affecting the foaming ingredients differently, with sucrose addition increasing E' and lowering the interfacial phase angle of std-EWP and hw-EWP, while decreasing E' and increasing the phase angle of WPI. Previous work has established that increases in E' and/or decreases in interfacial phase angle correlate with increased τ_0, and this was also found to be true within either WPI or EWP-based ingredients, but not true across solution types. Additionally, the capacity of these ingredients to impart high values of interfacial elasticity upon dilution from the foaming concentration (10%, w/v for all ingredients) seemed to be important for imparting improved foaming performance, i.e. increased τ_0 and resistance to drainage. That is, E' of both EWP-based ingredients *increased* upon dilution from 10% (w/v) protein, whereas E' of adsorbed WPI interfaces *decreased* upon dilution from 10% (w/v) protein. Interfacial data collected for purified β-lg and ovalbumin, the primary proteins found in WPI and EWP, respectively, revealed differing behavior than seen in their respective commercial preparations. These differing behaviors emphasize the importance of utilizing identical materials for foam and interfacial measurements, while also establishing protein concentration and measurement-time effects during interfacial rheology, if interfacial rheological measurements are to be effectively related to actual foam properties.

Acknowledgements

Paper No. FSR 05-21 of the Journal Series of the Department of Food Science, NCSU, Raleigh, NC 27695-7624. Support from the North Carolina Agricultural Research Service, Dairy Management Inc. and the Southeast Dairy Foods Research Center is gratefully acknowledged. Thanks to Davisco Foods International, Inc. and Primera Foods for supplying protein. The use of trade names in this publication does not imply endorsement by the North Carolina Agricultural Research Service of the products named nor criticism of similar ones not mentioned.

References

[1] G.M. Campbell, E. Mougeot, Trends Food Sci. Technol. 10 (1999) 283.
[2] E. Dickinson, Colloid Surf. B-Biointerfaces 15 (1999) 161.
[3] P.J. Wilde, Curr. Opin. Colloid Interface Sci. 5 (2000) 176.
[4] P.J. Halling, Crit. Rev. Food Sci. 15 (1981) 155.
[5] H.M. Zhu, S. Damodaran, J. Food Sci. 59 (1994) 554.
[6] M.R.R. Nino, J.M.R. Patino, Ind. Eng. Chem. Res. 41 (2002) 1489.
[7] D. Guzey, D.J. McClements, J. Weiss, Food Res. Int. 36 (2003) 649.
[8] J.R. Wendorf, C.J. Radke, H.W. Blanch, Biotechnol. Bioeng. 87 (2004) 565.
[9] M.G. Semenova, A.S. Antipova, L.E. Belyakova, Curr. Opin. Colloid Interface Sci. 7 (2002) 438.
[10] T.G. Mason, Curr. Opin. Colloid Interface Sci. 4 (1999) 231.
[11] C.W. Pernell, E.A. Foegeding, C.R. Daubert, J. Food Sci. 65 (2000) 110.
[12] C.W. Pernell, E.A. Foegeding, P.J. Luck, J.P. Davis, Colloids Surf. A-Physicochem. Eng. Asp. 204 (2002) 9.
[13] P.J. Luck, N. Bray, E.A. Foegeding, J. Food Sci. (2002).
[14] R.K. Prud'homme, S.A. Khan, in: R.K. Prud'homme, S.A. Khan (Eds.), Foams, Marcell-Dekker, Inc., New York, 1996, pp. 217–241.
[15] H.M. Princen, A.D. Kiss, J. Colloid Interface Sci. 128 (1989) 176.
[16] Y. Hemar, D.S. Horne, Langmuir 16 (2000) 3050.
[17] K. Lau, E. Dickinson, J. Food Sci. 69 (2004) E232.
[18] T.D. Dimitrova, F. Leal-Calderon, Adv. Colloid Interface Sci. 108–109 (2004) 49.
[19] D.M.A. Buzza, C.Y.D. Lu, M.E. Cates, J. Phys. II 5 (1995) 37.
[20] D.A. Edwards, D.T. Wasan, in: R.K. Prud'homme, S.A. Khan (Eds.), Foams, Marcell-Dekker, Inc., New York, 1996, pp. 189–215.
[21] J.P. Davis, D. Doucet, E.A. Foegeding, J. Colloid Interface Sci. 288 (2005) 412.
[22] J.P. Davis, E.A. Foegeding, J. Food Sci. 69 (2004) C404.
[23] J.P. Davis, E.A. Foegeding, F.K. Hansen, Colloid Surf. B-Biointerfaces 34 (2004) 13.
[24] V. Lechevalier, T. Croguennec, S. Pezennec, C. Guerin-Dubiard, M. Pasco, F. Nau, J. Agric. Food Chem. 51 (2003) 6354.
[25] A.H. Martin, K. Grolle, M.A. Bos, M.A. Stuart, T. van Vliet, J. Colloid Interface Sci. 254 (2002) 175.
[26] F. Gauthier, S. Bouhallab, A. Renault, Colloid Surf. B-Biointerfaces 21 (2001) 37.
[27] S. Roth, B.S. Murray, E. Dickinson, J. Agric. Food Chem. 48 (2000) 1491.
[28] S. Pezennec, F. Gauthier, C. Alonso, F. Graner, T. Croguennec, G. Brule, A. Renault, Food Hydrocolloids 14 (2000) 463.
[29] A.S. Antipova, M.G. Semenova, L.E. Belyakova, Colloid Surf. B-Biointerfaces 12 (1999) 261.
[30] M.R.R. Nino, P.J. Wilde, D.C. Clark, F.A. Husband, J.M.R. Patino, J. Agric. Food Chem. 45 (1997) 3016.
[31] M. Hammershoj, A. Prins, K.B. Qvist, J. Sci. Food Agric. 79 (1999) 859.
[32] C.C. Sanchez, S.E.M. Ortiz, M.R.R. Nino, M.C. Anon, J.M.R. Patino, Langmuir 19 (2003) 7478.
[33] N.Q. Dzuy, D.V. Boger, J. Rheol. 29 (1985) 335.
[34] J.F. Steffe, Rheological Methods in Food Process Engineering, second ed., Freeman Press, East Lansing, Michigan, 1992, pp. 243–250.
[35] L.G. Phillips, J.B. German, T.E. Oneill, E.A. Foegeding, V.R. Harwalkar, A. Kilara, B.A. Lewis, M.E. Mangino, C.V. Morr, J.M. Regenstein, D.M. Smith, J.E. Kinsella, J. Food Sci. 55 (1990) 1441.
[36] F.K. Hansen, J. Colloid Interface Sci. 160 (1993) 209.
[37] R. Wustneck, B. Moser, G. Muschiolik, Colloid Surf. B-Biointerfaces 15 (1999) 263.
[38] R. Myrvold, F.K. Hansen, J. Colloid Interface Sci. 207 (1998) 97.
[39] D.Y. Kwok, W. Hui, R. Lin, A.W. Neumann, Langmuir 11 (1995) 2669.
[40] L.G. Phillips, S.T. Yang, W. Schulman, J.E. Kinsella, J. Food Sci. 54 (1989) 743.
[41] F.K. Hansen, R. Myrvold, J. Colloid Interface Sci. 176 (1995) 408.
[42] C.J. Beverung, C.J. Radke, H.W. Blanch, Biophys. Chem. 81 (1999) 59.
[43] P. Chen, R.M. Prokop, S.S. Susnar, A.W. Neumann, in: D. Mobius, R. Miller (Eds.), Proteins at Liquid Interfaces, Elsevier, Amsterdam, 1998, pp. 303–339.
[44] P. Wilde, A. Mackie, F. Husband, P. Gunning, V. Morris, Adv. Colloid Interface Sci. 108–109 (2004) 63.
[45] J.C. Lee, S.N. Timasheff, J. Biol. Chem. 256 (1981) 7193.
[46] F. MacRitchie, in: D. Mobius, R. Miller (Eds.), Proteins at Liquid Interfaces, Elsevier, Amsterdam, 1998, pp. 149–177.

[47] P.J. Wilde, D.C. Clark, in: G.M. Hall (Ed.), Methods of Testing Protein Functionality, Blackie Academic & Professional, London, 1996, pp. 110–152.
[48] M.A. Bos, T. van Vliet, Adv. Colloid Interface Sci. 91 (2001) 437.
[49] J. Benjamins, E.H. Lucassen-Reynders, in: D. Mobius, R. Miller (Eds.), Proteins at Liquid Interfaces, Elsevier, Amsterdam, 1998, pp. 341–384.
[50] E.H. Lucassen-Reynders, Food Struct. 12 (1993) 1.
[51] J.M.R. Patino, M.R.R. Nino, C.C. Sanchez, J. Agric. Food Chem. 47 (1999) 3640.
[52] P. Reiser, G.G. Birch, M. Mathlouthi, in: M. Mathlouthi, P. Reiser (Eds.), Sucrose Properties and Applications, Blackie Academic and Professional, Glasgow, 1995, pp. 186–222.