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Pendant drop tensiometry for the evaluation of the foaming properties of milk-derived proteins

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ABSTRACT

Aim of the present study was to investigate the relationship between parameters derived from pendant drop tensiometry and foaming properties of milk-derived proteins. Foaming time and foam stability of solutions of whey protein isolate and two different whey protein hydrolysates with varying protein content were analysed. Pendant drop tensiometry was used to determine the surface elasticity and different parameters from a modified dynamic surface tension measurement to characterise protein adsorption to the air-water interface. A modified pendant drop technique allowed the characterisation of the surface occupation of proteins for very fast processes like air bubble stabilisation during foaming. Principal component analysis revealed a close relation between foaming time and parameters from dynamic surface tension measurement (lag time for protein adsorption to the interface, slope of the regression line for the change in surface tension) as well as foam stability with parameters derived from interfacial rheology (surface dilatational modulus as well as elastic and viscous components, phase angle). Therefore pendant drop tensiometry proved to be a valuable tool for the characterisation and prediction of the foaming properties and foam stability of protein solutions.

1. Introduction

Foam is commonly defined as a colloidal dispersion of a gas phase in a liquid phase. The volume of the dispersed phase (air) is generally large in comparison with the volume of the continuous phase (water). The large interfacial area and the difference in the density of the two phases result in a high interfacial tension and hence in a very unstable system. The function of proteins in foams is to stabilize the system by reducing the interfacial tension. Foamability (sometimes also referred to as foaming capacity) can be characterised through the time required to gain a specified foam volume (Marinova et al., 2009). Foam stability is related to the time a foam preserves its properties and can be characterised e.g. by the drainage of liquid phase from the foam over time (Marinova et al., 2009).

Due to their amphiphilic macromolecular character globular proteins, such as whey proteins, show a good surface activity and thus have a stabilizing effect on foams and emulsions (Mahmoudi, Gaillard, Boué, Axelos, & Riaublanc, 2010). The foaming properties of globular proteins are determined by their rate of diffusion and rate of adsorption to the interface, the ability to unfold their globular molecular structure and their aggregation at the interface (Borcherding, Lorenzen, Hoffmann, & Schrader, 2008). However, whey protein fractions differ in their adsorption behaviour. The unfolding of the molecular structure, respectively the tertiary structure, during adsorption of α-lactalbumin is taking place more rapidly than for β-lactoglobulin (Cornec, Cho, & Narsimhan, 1999).

Enzymatic hydrolysis is a suitable mean to modify the foaming properties of proteins (Davis, Doucet, & Foegeding, 2005). Due to enzymatic hydrolysis of globular proteins, e.g., whey proteins, a reduction of the molecular size by structural disintegration occurs, which is accompanied by an exposure of hydrophobic groups (Creusot, Gruppen, van Koningsveld, deKruif, & Voragen, 2006). The molecular weight profile and composition of the different fractions depends on the degree of hydrolysis, the type of enzyme used, the environmental conditions and the pre-treatment of the substrate (Althouse, Dinakar, & Kilara, 1995; González-Tello, Camacho, Jurado, Páez, & Guadix, 1994; Ipsen et al., 2001; Peña-Ramos & Xiong, 2001). If the purpose of the modification is to improve foaming capacity and foam stability, a low degree of hydrolysis is favourable (Conde & Rodriguez Patino, 2007). The smaller molecules maintained by controlled hydrolysis of whey protein isolates show improved foaming properties compared to non-hydrolysed isolates due to their fast migration to the air-water interface and due to a more rapid unfolding of their molecule

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structure (Althouse et al., 1995). Hydrolysed β-lactoglobulin (degree of hydrolysis 19–26 %) formed stronger viscoelastic films at the air-water interface in comparison with films prepared from unmodified β-lactoglobulin. Furthermore hydrolysis led to an increase in foam overrun, according to Ipsen et al. (2001) presumably caused by the exposure of hydrophobic segments.

Protein adsorption processes on a short time scale seem to be diffusion controlled, in contrast to an occurring energy barrier which limits surfactant adsorption during long time observations (Cornec et al., 1999). Therefore dynamic surface tension measurement is an important analytical tool to determine the foaming properties of surfactants (Marinova et al., 2009). A rapid decrease of surface tension indicates a fast adsorption of the surfactants to the surface and hence a fast stabilisation of the dispersed phase (e.g. air bubbles) against coalescence. In different studies on foaming properties of proteins surface tension has been analysed using the Wilhelmy plate method (Pozani, Doxastakis, & Kiosseoglou, 2002; Rodríguez Patino et al., 2007), the duNoüy ring method (Horiuchi, Fukushima, Sugimoto, & Hattori, 1978; Ridout, Mackie, & Wilde, 2004) or pendant drop tensiometry (Conde & Rodriguez Patino, 2007). Surface tension measurement at interfaces via video-enhanced pendant drop tensiometry is considered as a very accurate method (Lin, McKeigue, & Maklarelli, 1990). However, all these techniques are based on long-term observations, which do not necessarily reflect the diffusion and adsorption behaviour in very fast processes like e.g. foam formation. To the best of our knowledge, the work of Marinova et al. (2009) is the only literature available providing data on dynamic surface tension measurements on a fairly short time scale (10 s) using a pendant drop tensiometer. Drusch, Hamann, Berger, Serfert and Schwarz (in press) recently a developed double syringe system attached to an automated drop tensiometer to inject protein sample solution into a drop of water to display surface tension development due to protein adsorption in very fast processes like droplet formation after atomisation during spray drying.

The aim of the present study was to investigate the relationship between parameters derived from pendant drop tensiometry (dynamic surface tension measurement, interfacial rheology via volume oscillation) and foaming properties of milk proteins. Whey protein isolate and hydrolysed whey proteins with different degree of hydrolysis are used as model compounds with relevance for industrial applications. It was hypothesized that surface accumulation and thus change in surface tension is related to foamability as well as parameters from interfacial rheological measurements with foam stability. Molecular weight profile of the proteins was characterised using SDS-PAGE. Foaming experiments were performed according to the method described by Borcherding et al. (2008). Dynamic surface tension as well as surface elasticity was analysed using pendant drop tensiometry.

2. Materials and methods

Whey protein isolate and whey protein hydrolysates were provided by Fonterra Europa GmbH, Hamburg, Germany. Solutions of whey protein isolate (WPI) and whey protein hydrolysates (WPH) with different degree of hydrolysis (DH; 11.0% and 18.1%) were prepared in 0.2 M phosphate buffer pH 7.0 as described in other studies (Carrera Sánchez & Rodríguez Patino, 2005; Martin, Grolle, Bos, Stuart, & van Vliet, 2002; Rodriguez Niño, Sánchez, & Rodriguez Patino, 1999). Reproducibility of all analysis on foaming properties and reproducibility of the pendant drop tensiometry was analysed through calculation of the coefficient of variation for a 15-fold determination of different samples including the intraday variation (three analyses per day) and the day-to-day variation (five days).

2.1. SDS-PAGE of whey protein isolate and whey protein hydrolysates

Sodium dodecyl sulphate polyacrylamide gel eletrophoresis (SDS-PAGE) was performed using a reducing buffer system (Roti-Load 1) containing bromophenol blue, glycerine and mercaptoethanol (Carl Roth, Germany, K929.1). The running buffer for this analysis was Rotiphorese 10 × SDS-PAGE (Carl Roth, Germany, 3060.1). The protein fractions with different total protein loads (30 μg, 40 μg and 150 μg protein/15 μl applied protein solution to the gel) were separated on 12% SDS-PAGE Minigel (Bio-Rad, #456-1043) and 18% SDS-PAGE gel and stained with Coomassie blue (Carl Roth, Germany, A152.1). Low-range protein ladder markers were used as reference material (Fermentas, Germany, SM1891 und SM1861).

2.2. Characterisation of the foaming properties of whey protein isolate and whey protein hydrolysates

Foamability and foam stability of protein solutions was studied via a specifically designed foaming apparatus (Fig. 1) as described by Borcherding et al. (2008). The foaming apparatus consists of the glass plungers A1 and A2, with A1 having a porous frit (pore size 10–16 μm) in the bottom of the vessel. The lower aperture of A1 is connected to a pressure regulator (diameter of output line = 9 mm) followed by a compressed air plug. In order to determine the foamability of the samples 250 ml of solution were given into foaming apparatus A1. A2 was put on top of A1 and the compressed air supply was started with a constant pressure of 3.5×10^4 Pa. Foaming was continued until the foam volume reached 200 ml in A2 (according to a total volume of solution and foam in A1 and A2 of 650 ml). The foaming time t_f to gain this volume was recorded as a specific foamability parameter of each solution. Immediately after the volume was reached A2's upper aperture was capped and A2 was put on top of the foam stability apparatus A3. At the bottom of A3 another porous frit (pore size 100–160 μm) is embedded to retain the foam and let the drainage pass through. The drainage was recorded every minute for a time scale of 10 min. The drainage D was determined by differential measurement of weight according to Eq. (1):

$$D[\%] = \left(\frac{\text{mass}_{\text{liquid}}}{\text{mass}_{\text{foam}}}\right) \cdot 100 \quad (1)$$

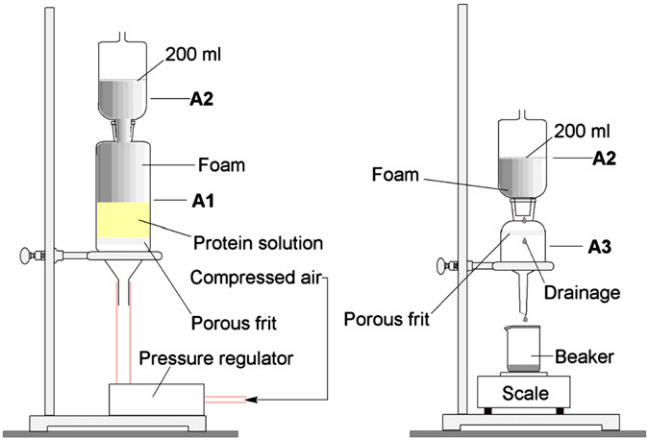

Fig. 1. Apparatus for the determination of foamability (left) and foam stability (right) according to Borcherding et al., (2008).

Differences between the samples with respect to drainage were highest after five minutes and therefore these data are reported as D_5. Foam weight m_f was calculated from the sum of the weights of A2 and A3 filled with sample plus the drainage minus the weight of the apparatus A2 and A3 itself. All foaming experiments were carried out in triplicate with protein solutions adjusted to a temperature of 22 ± 0.5 °C.

2.3. Dynamic surface tension measurement of whey protein isolate and whey protein hydrolysates

The determination of the surface tension $\sigma(t)$ was based on the shape analysis of a pendant drop according to the Young–Laplace-equation:

$$\Delta P = \sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \quad (2)$$

The surface tension σ can be calculated, if R_1 and R_2, the two principal radii of curvature of the surface, and ΔP, the pressure difference across the interface, are known. Surface pressure π is calculated by $\pi = \sigma_0 - \sigma$ with σ_0 as the surface tension of the empty surface (water; $\sigma_0 = 72.8$ mN/m).

In the present study, the measurements were performed using an automated drop tensiometer OCA20 (Dataphysics GmbH, Germany). Fig. 2 shows a schematic view of the assembly. Within the temperature controlled chamber a drop of distilled water (V = 15μl ± 0.25) is produced manually through the large opening (d = 1.65 mm) of the 2-channel needle (Fig. 2). 2 μl of the sample solution is injected subsequently into the drop of water through the small opening (d = 0.51 mm) via the automatic dosing unit with a dosing rate of 20 μl/s (Drusch et al., in press). The change in drop shape is monitored through a high speed frame grabber (200 frames/s).

This technique provides an insight into the adsorption process of surfactants to an initially empty surface. The underlying model has been established by Ward and Tordai, 1946. Based on this model the lag time and the initial slope k in the π–$t^{1/2}$-diagram (Fig. 3 top) can be used to characterise the initial diffusion of the protein molecules to the empty surface and its incorporation. If the lag time is short and k is high it can be supposed the surfactants are reaching the surface faster and stabilisation against bubble coalescence occurs.

Dynamic surface tension measurement was also used to determine the critical interfacial concentration (CIC) of the proteins in solution. Knowledge about the CIC was necessary for oscillation experiments. At the CIC the minimum surface tension is reached and it is not possible to decrease surface tension any further by raising the concentration, since a full coverage of the surface with surfactant is reached. Equilibrium surface tension of all protein solutions was determined for a protein content ranging from 0.01 to 1.0 wt%. The surface tension for each protein solution was plotted versus the concentration. Two tangents were fitted and the intersection of theses tangents was considered to represent the CIC (Fig. 3 bottom).

2.4. Dilatational rheology of whey protein isolate and whey protein hydrolysates

The experiments were carried out using the same apparatus as for dynamic surface tension measurement except of replacing the automatic dosing unit with an oscillating drop generator unit (ODG20, Dataphysics, Germany). Sinusoidal oscillations at a constant angular frequency f (0.1 Hz) with a volume amplitude of 10% were conducted, resulting in a change of surface area (ΔA/A). Each measurement consisted of 10 cycles.

The surface viscoelastic parameters, i.e., surface dilatational modulus, E*, its elastic, E′, and viscous, E″, components and the phase angle (Φ) were derived from the change in surface tension σ (dilatational stress) resulting from a small change in surface area (dilatational strain) (Lucassen & van den Temple, 1972). The surface dilatational modulus is a complex quantity and consists of real and imaginary parts. The real component of the dilatational modulus or storage component is the dilatational elasticity, E′. The imaginary part of the dilatational modulus or loss component is the surface dilatational viscosity, E″. For a perfectly elastic material, stress and strain are in phase ($\varphi = 0$) and the imaginary term is zero, accordingly for a perfectly viscous material $\varphi = 90°$ and the real part is zero (Conde & Rodriguez Patino, 2005; Rodríguez Patino, Rosario Rodríguez Niño, & Carrera Sánchez, 1999). The loss factor tan δ expresses the ratio of the viscous and elastic part of the

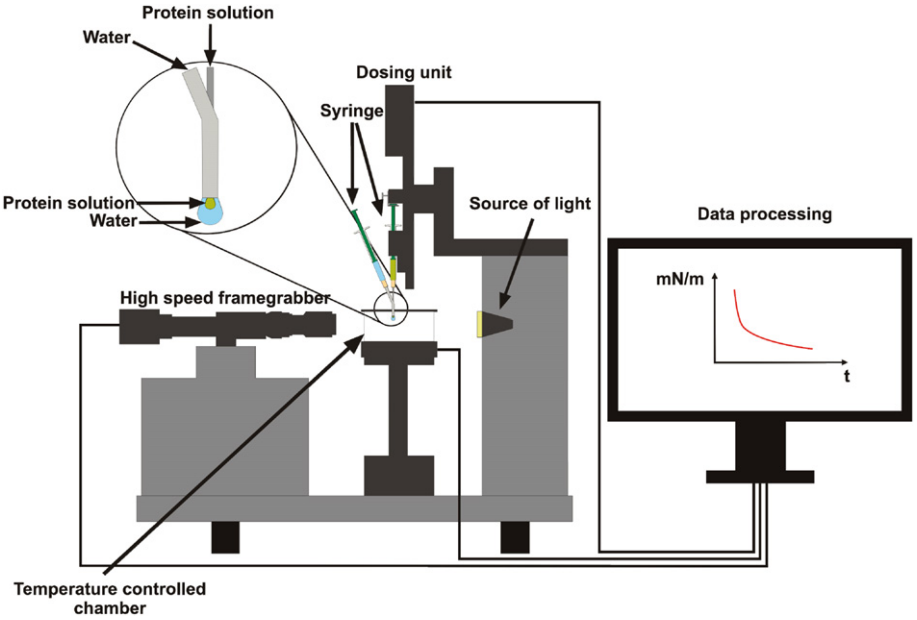

Fig. 2. Pendant drop tensiometer with modified dosing system as described by Drusch et al. (in press)

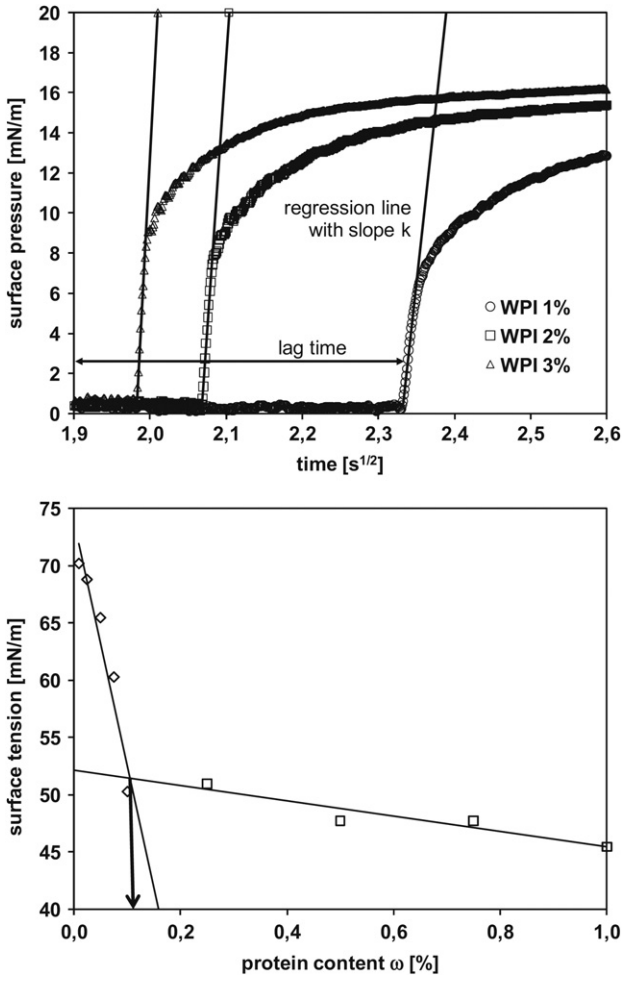

Fig. 3. (top) Plot of surface pressure vs. $t^{1/2}$ of WPI including the slope k (bottom) determination of the critical interfacial concentration (CIC) for WPH DH = 11%.

viscoelastic deformation behaviour (tan δ = E″/E′). The closer the values for tan δ are to zero, the more elastic the surfactant layer is.

All experiments were carried out at least with six replicates with protein solutions at room temperature (22.0 ± 0.5 °C). The temperature controlled chamber of the apparatus was adjusted to 22.0 °C. Before the oscillation measurement was started one oscillating cycle was conducted to ensure total surface coverage with protein.

2.5. Statistics

In the present study, principal component analysis (PCA) was used to: (a) explore relations between analytical parameters, (b) identify most important properties, which characterize the samples, and (c) visualize them in a simpler way. PCA is a data reduction technique used to identify a small set of variables that account for a large proportion of the total variance in the original variables. The dataset used was a matrix composed of 10 variables (k: slope of the regression line of the change in surface tension; t_f: foaming time, m_f: foam weight; D_5: liquid drainage after 5 min; E*: surface dilatational modulus; E′: elastic component of the surface dilatational modulus; E″ viscous component of the surface dilatational modulus; Φ: phase angle) Each sample has been analyzed at least in double. Principal component analysis has been performed by using the correlation matrix. This practice is recommended all the times the variables have different units of measurement. The result is a principal component analysis which is independent from the variables scale. All calculation has been performed by the software Minitab®, ver. 14.0.

3. Results and discussion

3.1. Molecular weight profile of whey protein isolate and whey protein hydrolysates

Fig. 4 shows the electrophoretograms of low molecular weight markers (#SM1861 and #SM1891, lane 1 and 2) and proteins (WPI: lane 9–10; WPH 11% DH: lane 3–5; WPH 18.1% DH: lane 6–8). Whey protein isolate (lane 8–10) shows light bands at approximately 60–70 and 35 kDa. According to Monahan, German, and Kinsella (1995) the 60–70 kDa band shows bovine serum albumin (BSA), which showed a MW of 66.2 kDa in their work. The same authors found dimers of α-lactalbumin and β-lactoglobulin ranging between 28.4 and 36.8 kDa, which is supposed to be the band at 35 kDa in the present study. In addition mixed dimers may occur. Additional bands found at 15 and 12.5 kDa, which were are considered to be β-lactoglobulin and α-lactalbumin.

The molecular weight profil of the WPH with a DH of 11% showed just light bands in the molecular weight range from 11 to 2 kDa. In the electrophoretogramm of the WPH DH = 18.1% no bands could be identified after Coomassie staining. Based on data from a previous study (data not published) using the same hydrolysate (but a different lot), where silver staining was applied, and data from the literature (González-Tello et al., 1994) it can be stated that the bulk of peptides was in the range between 1 and 3 kDa at this degree of hydrolysis.

3.2. Foamability and dynamic surface tension of whey protein isolate and whey protein hydrolysates

With a coefficient of variation of less than 10% the reproducibility of the foaming time t_f was good. Dynamic surface tension experiments showed a coefficient of variation lower than 5%. The results for foaming time t_f (foamability) and dynamic surface tension measurement are displayed in Table 1. The foam weight m_f increased with increasing protein content ω only for WPH for a DH = 11.0%, but no trend with respect to m_f can be found for the other proteins. Foams prepared from WPI exhibited significantly higher foam weights than the hydrolysates. This could be due to

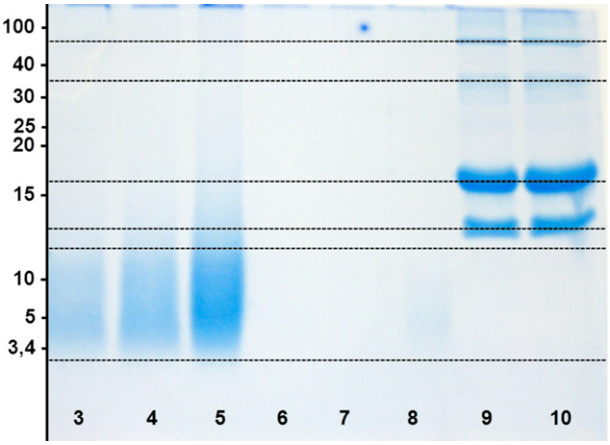

Fig. 4. SDS-PAGE of whey protein isolate (lane 9–10), whey protein hydrolysate (DH 18,1%: lane 6–8; DH 11%: lane 3–5).

Table 1
Data from experiments on foamability of protein solutions and corresponding data from dynamic surface tension measurements (DH: degree of hydrolysis; k: slope of the regression line of the change in surface tension; t_f: foaming time, m_f: foam weight).

Protein	DH [%]	Protein content [wt%]	Lag phase [s]	k [mN·m^{-1}·s$^{1/2}$]	t_f [s]	m_f [g]
WPI	0	1	5.5 ± 0.3	19.5 ± 0.9	36.7 ± 0.5	30.7 ± 0.2
WPI	0	2	4.3 ± 0.2	25.6 ± 0.2	72.5 ± 1.1	30.1 ± 0.5
WPI	0	3	4.0 ± 0.1	31.5 ± 0.5	77.0 ± 1.4	31.8 ± 0.7
WPH	11.0	1	2.1 ± 0.0	41.6 ± 0.0	61.5 ± 0.5	10.7 ± 0.2
WPH	11.0	2	1.7 ± 0.1	43.6 ± 0.1	111 ± 1.7	19.3 ± 0.5
WPH	11.0	3	1.5 ± 0.0	55.5 ± 0.3	144 ± 5.0	19.5 ± 0.5
WPH	18.1	1	1.8 ± 0.0	37.2 ± 0.1	57.5 ± 2.5	22.7 ± 0.2
WPH	18.1	2	1.7 ± 0.0	45.9 ± 0.6	87.5 ± 1.5	20.3 ± 0.0
WPH	18.1	3	1.3 ± 0.0	51.5 ± 0.0	102 ± 4.0	21.6 ± 0.4

intact globular whey proteins with higher molecular weight or even aggregates of those acting as barriers in the thin films between the bubbles and in the plateau border region, entrapping more liquid in the foam. A similar observation has been reported by Rullier, Novales, and Axelos (2008) for heat-induced aggregates of proteins in foam. The foaming time t_f increased with increasing ω, probably due to a faster stabilisation of the bubbles being released from the pores of the porous frit during the foaming process. A fast stabilisation of bubbles is associated with a low bubble volume and thus more time is required to achieve a defined foam volume. Furthermore, less coalescence occurs due to the excess of protein being available to cover the newly developed surface fast (Carrera Sánchez & Rodríguez Patino, 2005; Marinova et al., 2009).

In the present study, for the first time a more detailed view on the dynamics of the initial change in surface pressure is reported. With a protein content of 1–3 wt%, all experiments were performed at a protein content well above the critical interfacial concentration for the pendant drop, which amounted to 0.10–0.13 % for the three proteins. At a protein content above the CIC a slight decrease of the surface equilibrium tension occurred, which indicates the presence of surface-active impurities in the commercial protein hydrolysate. The slope of the tangent k increased with increasing protein content ω in solution (Table 1). A similar observation has been reported in studies observing the surface pressure increase in long-term measurements (Miller, Aksenenko, Fainerman, & Pison, 2001; Rodríguez Patino et al., 2007). It is generally accepted, that a reduction of the molecular mass of whey proteins is associated with a better accessibility of hydrophobic segments of the molecule, an increase in the amphiphilic character of the molecule and a higher surface activity. In the present study, this conclusion is supported by a decrease of the lag phase with increasing protein content and degree of hydrolysis (Table 1).

3.3. Foam stability and dilatational rheology of whey protein isolate and whey protein hydrolysates

The results on foam stability of foams (drainage, D_5) prepared from the different protein solutions and data from the experiments on dilatational rheology are shown in Table 2. Reproducibility of both, experiments on foam stability and dilatational rheology experiments, was always better than 10%. Five minutes was chosen as the time, where the most infinite differences occurred in liquid drainage (D_5) from the foams. D_5 decreased with increasing protein content for all proteins and ranged from 50.8 to 76.8 % for WPI (protein content: 3 wt%) and WPH with a DH of 11.0 (protein content: 1 wt%), respectively. It is hypothesized that foam stability is partly associated with an increase in foam dispersity, i.e.: smaller bubble radius) (Exerowa & Kruglyakov, 1998). This observation is supported by former studies (Davis et al., 2005; Marinova et al., 2009; Rodríguez Patino et al., 2007). Furthermore, drainage is linked to the viscosity of the continuous phase. As a consequence of an increase in viscosity liquid flow within the lamellae and the border regions is slower and the liquid is retained inside the foam (Carp, Wagner, Bartholomai, & Pilosof, 1997; Wierenga, van Noréla, & Basheva, 2009). In the present study with a protein content ranging from 1 wt% to 3 wt% a significant increase in the viscosity of the bulk phase is not likely. It is hypothesized that aggregation of low molecular weight constituents results in a change of viscosity within the lamellae. Rullier et al. (2008) postulated a peptide-mediated aggregation of β-lactoglobulin to explain an increase in foam stability, if hydrolysed whey proteins are used. Spellman, Kenny, O'Cuinn, and Fitzgerald, 2005 showed that the activity of a glutamyl-endopetidase was responsible for the formation of peptides prone to aggregation during production of commercial whey protein hydrolysate. In the present study differences in the molecular weight profile and composition of the peptides as well as hydrophobicty of the peptides in the aggregation behaviour may explain the increase in surface dilatational modulus for the whey protein hydrolysate with a DH of 18% in the present study.

One destabilisation process in foams is the foam coarsening (disproportionation) due to gas diffusion between bubbles of different sizes and hence different capillary pressure. The surface dilatational viscoelasticity of surfactant layers reflects the force working against the shrinkage of the bubbles (Dickinson, 2006). Globular proteins, e.g., β-lactoglobulin, irreversibly adsorb at the air-water interface and form highly viscoelastic films, thus they are suitable to stabilise foams in long-term (Dickinson, 2006). In the present study, the surface dilatational modulus E* and both E′ and E″ increased with increasing protein content for samples containing WPH with a DH of 18.1%. With 95.6, 78.2 and 52.0 mN/m, WPH DH = 18.1% (protein content: 3 wt%) showed the highest values of all analysed proteins for E*, E′ and E″, respectively. For hydrolysed proteins, D_5 decreased with increasing protein content.

Table 2
Data from experiments on foam stability of protein solutions and corresponding data from dilatational rheology measurements (DH: degree of hydrolysis; D_5: liquid drainage after 5 min; E*: surface dilatational modulus; E′: elastic component of the surface dilatational modulus; E″ viscous component of the surface dilatational modulus; Φ: phase angle).

Protein	DH [%]	Protein content [wt%]	D_5[%]	E* [mN·m^{-1}]	E′ [mN·m^{-1}]	E″ [mN·m^{-1}]	Φ [°]	tan Φ
WPI	0	1	61.5 ± 1.2	69.2 ± 0.6	62.9 ± 0.5	28.4 ± 0.2	24.1 ± 0.2	0.45
WPI	0	2	61.2 ± 1.5	70.4 ± 0.7	64.0 ± 0.6	29.4 ± 0.4	24.6 ± 0.4	0.46
WPI	0	3	50.8 ± 0.8	67.8 ± 0.6	60.6 ± 0.6	30.3 ± 0.4	26.5 ± 0.3	0.50
WPH	11.0	1	76.8 ± 2.6	57.6 ± 0.1	52.3 ± 0.0	27.5 ± 0.0	26.2 ± 0.2	0.50
WPH	11.0	2	71.2 ± 0.5	51.0 ± 0.4	44.4 ± 0.4	25.2 ± 0.2	29.6 ± 0.0	0.57
WPH	11.0	3	66.8 ± 0.1	47.8 ± 0.0	40.2 ± 0.1	26.4 ± 0.3	33.2 ± 0.2	0.66
WPH	18.1	1	71.8 ± 0.9	84.1 ± 0.2	72.3 ± 0.6	42.9 ± 1.5	30.7 ± 1.1	0.60
WPH	18.1	2	59.6 ± 0.7	86.2 ± 2.4	76.1 ± 1.8	40.4 ± 1.6	28.0 ± 0.4	0.53
WPH	18.1	3	51.0 ± 0.3	95.6 ± 0.0	78.2 ± 0.3	52.0 ± 0.7	33.3 ± 0.1	0.66

Furthermore, with increasing protein content and DH values for Φ and tan Φ tended to increase.

Martin et al. (2002) observed just a weak correlation between surface rheological properties and foam stability. The correlations observed were explained case-by-case, as a function of the prevalent instability mechanisms of the foam involved. However, no multivariate approach has been used at that time. As shown in Fig. 5 samples prepared with the different proteins, WPI and both WPHs could clearly be separated. Principal component 1 (51% of the total variance) separated the samples containing hydrolysed protein from the samples containing whey protein isolate. Foam weight, foaming time, lag phase and the slope of the regression line contribute to the PC1. With R^2 ranging from 0.69 to 0.94, all these variables characterise the foamability and are highly correlated with each other (Table 3). The samples prepared from the different whey protein hydrolysates are separated via principal component 2 (32% of total variance). The loading plot shows that the distinction is based on the data on foam stability and data from interfacial rheology. The loading plot shows that rheological characteristics of the foams (E*, E′) are correlated with the drainage D_5 ($R^2 = 0.51$).

Until now surface shear viscosity (Alvarez Gomez & Rodriguez Patino, 2007) has been suggested for foam characterisation, since higher surface shear viscosities of protein solutions result in decreased drainage rates and thus in more stable foams. As reviewed by Ritacco, Cagna, and Langevin (2006) this analysis can be conducted by use of an oscillating disc apparatus. Analysis of disjoining and capillary pressure of foam films was recently used by Wierenga et al. (2009). Since in the present study foaming time t_f was associated with parameters from dynamic surface tension measurement (k) as well as foam stability (mass of liquid drainage, D_5) with parameters derived from interfacial rheology (E*, E′, E″) pendant drop tensiometry is a valuable tool for the characterisation of the foaming properties of protein solutions.

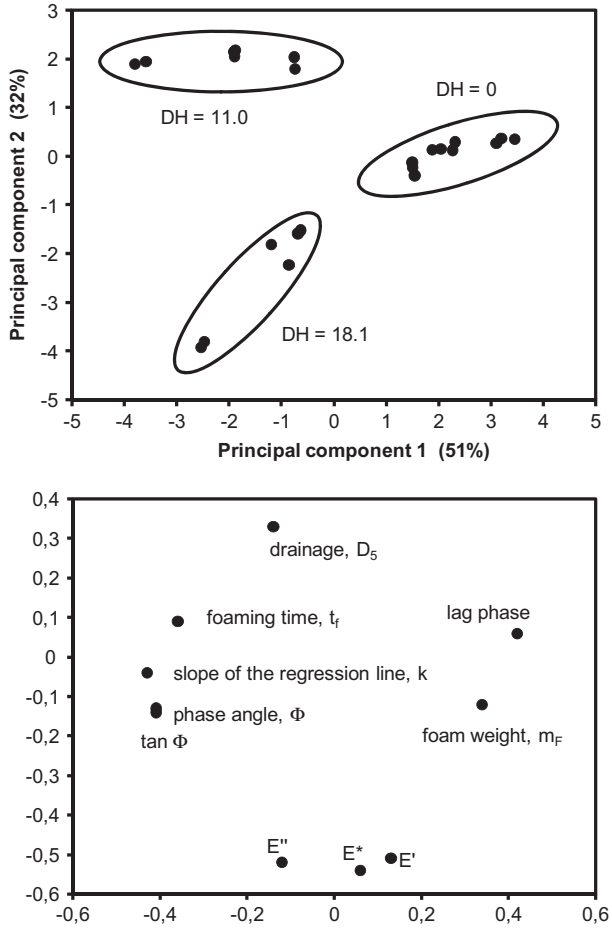

Fig. 5. Score plot and loading plot for the principal component analysis of foams prepared from different proteins at different concentrations.

Table 3
Correlation matrix for the results from pendant drop tensiometry and foaming experiments (k: slope of the regression line of the change in surface tension; t_f: foaming time, m_f: foam weight; D_5: liquid drainage after 5 min; E*: surface dilatational modulus; E′: elastic component of the surface dilatational modulus; E″ viscous component of the surface dilatational modulus; Φ: phase angle).

	Lag phase	k	t_f	m_f	D_5	E*	E′	E″	Φ
k	−0.94								
f_t	−0.69	0.81							
f_w	0.81	−0.75	−0.40						
D_5	−0.35	0.18	0.02	−0.66					
E*	−0.02	−0.06	−0.34	0.22	−0.51				
E′	0.12	−0.21	−0.47	0.30	−0.51	0.98			
E″	−0.38	0.33	−0.02	−0.08	−0.38	0.91	0.82		
Φ	−0.84	0.88	0.74	−0.52	0.08	0.08	−0.10	0.48	
tan Φ	−0.84	0.88	0.74	−0.52	0.08	0.07	−0.11	0.47	1.00

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