P-070 **Surface accumulation of caseinate and casein hydrolysate during spray-drying**

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INTRODUCTION AND OBJECTIVES

Recently, research started to focus on submicron structural aspects, additional structure modification within spray-dried microcapsule and the functionality of these microcapsules. For example, a concept of "in situ"-coating by accumulation of surface-active substances at the air water interface of a drying droplet has been introduced to increase microencapsulation efficiency (Elverssson and Millqvist-Fureby, 2006).

Aim of the present was to develop a method to characterise the accumulation of surface-active compounds in a droplet on a time-scale relevant for spray-drying
and to compare the results obtained with this methods with results from analysis of the particle surface composition.

MATERIALS AND METHODS

Sodium caseinate and casein hydrolysate were chosen as proteins. It was expected that the surface activity of the hydrolysed casein is higher than the surface activity of sodium caseinate due to the reduction in molecular weight.

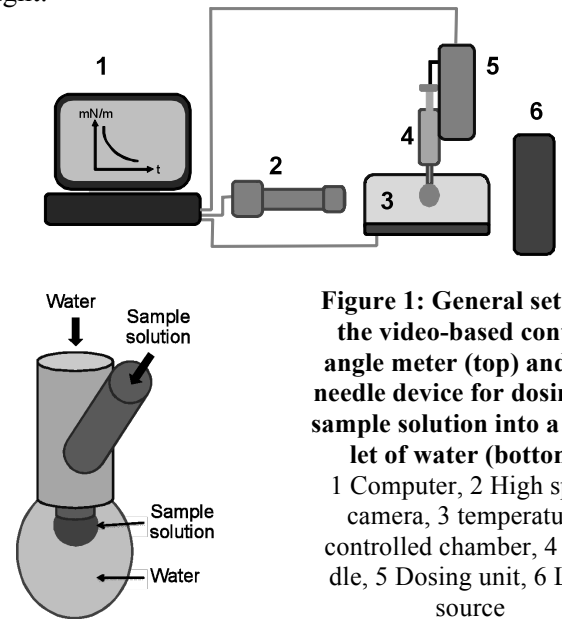

Figure 1: General setup of the video-based contact angle meter (top) and two needle device for dosing the sample solution into a droplet of water (bottom). 1 Computer, 2 High speed camera, 3 temperature-controlled chamber, 4 Needle, 5 Dosing unit, 6 Light source

Surface accumulation was determined by dynamic surface tension measurement using a video-based contact angle meter (OCA-20, Dataphysics Instruments GmbH, Filderstadt, Germany). The general setup of the instrument is given in Figure 1. The drop is generated at the tip of a needle using a dosing unit. A high speed frame grabber provides the possibility to acquire images of the drop at the tip of the needle with a frame rate of up to 200 images per second.

To monitor the changes in surface tension within this short time period, the experimental setup was modified as outlined in Figure 1. A first syringe with an outer diameter of 0.51 mm was laterally introduced into a second syringe with an outer diameter of 1.65 mm. A needle filled with distilled water was mounted onto the outer syringe and a droplet of 14 +/- 0.5 µl was manually generated at the tip of the syringe. A second needle was filled with the sample solution and mounted onto the automatic dosing system of the contact angle meter. A volume of 2 µl was injected into the water droplet at a dosing rate of 20 µl/sec.

The surface tension was calculated based on the drop shape through the Young–Laplace equation. Data evaluation was performed using the model of Ward and Tordai on the diffusion of proteins towards a planar interface (Ward and Tordai, 1946).

X-ray photoelectronspectroscopy (XPS) was performed using a XPS spectrometer (Omicron Full Lab) equipped with a A1 K_{α} X-ray source without monochromator.

RESULTS AND DISCUSSION

The performance of the dynamic surface tension measurement was significantly improved through modification of the experimental setup. Using the commercially available dosing unit a high dosing rate was required to generate a droplet in a time interval relevant for the atomisation of a liquid during spray-drying. At the time the droplet stabilises at the tip of the needle, the surface accumulation of the protein had already occurred. In contrast, when using the newly developed two needle system, the time required for generation of the protein containing droplet was reduced to approximately 100 ms.

When analysing the surface pressure at the air-water interface after injection of a solution of sodium caseinate or casein hydrolysate, for both proteins and all concentrations three different phases could be distinguished. At first, immediately after injection of the sample solution no change of surface pressure occurs. Depending on the protein concentration this so-called "lag phase" lasted for

approximately 600 to 1200 ms for sodium caseinate and 300-600 ms for casein hydrolysate (Table 1).

Thereafter a period characterised by a constant rate of increase in surface pressure as reflected by the slope of the regression line (k) for this time interval occurred in the present study. The lag time for caseinate in a concentration range between 0.1 and 0.25% was markedly higher than for casein hydrolysates in range 0.1 and 0.75 % (Table 1). In higher concentration (>0.5 %) the lag time for caseinate was clearly reduced, i.e. at higher concentration protein molecules start to accumulate at the interface in a shorter period of time.

Table 1 : Characterisation of the development of surface pressure at a spherical air-water interface over time after injection of sodium caseinate (SC) or casein hydrolysate (CH)

	Protein content [%]	lag time [$ms^{0.5}$]	Slope of the regression line (k) [$mN*m^{-1}/ms^{0.5}$]
SC	0.1	33.7	0.51
	0.25	36.8	2.59
	0.5	23.7	3.94
	0.75	25.8	7.88
	1.0	27.4	6.38
CH	0.1	25.3	1.04
	0.25	21.8	1.73
	0.5	20.7	4.84
	0.75	23.3	6.09
	1.0	15.7	4.51

As can be seen from Table 1, k increases up to a concentration of 0.75 % protein in the injected solution. At higher protein concentration molecular interactions, e.g. aggregation as it is described for caseinate, may hinder the process of diffusion and reduce k. A second possible reason for the decrease of k is that at a high protein concentration the incorporation of protein arriving at the interface is hindered and slows down the increase of the surface pressure. For both proteins at a concentration the k decreases when concentration is further increased to 1 % . The drop of k may indicate that proteins start to build up a multiple layer and do less penetrate into the protein covered surface. The similar behaviour of caseinate and casein hydrolysate, and thus the importance of other parameters apart from the molecular weight to characterise the surface activity, is supported by the concentration-dependency of k for the two proteins. I.e. hydrolysis does not necessarily lead to a reduction of the hydrodynamic radius of the casein micelle, since unfolded amino acid chains can still be bound to the core micelle through peptide bonds (Liu, 2007).

XPS revealed that both proteins accumulate at the air-water interface after spray-drying. At similar protein concentration the surface coverage with casein hydrolysate was always higher compared to sodium caseinate.

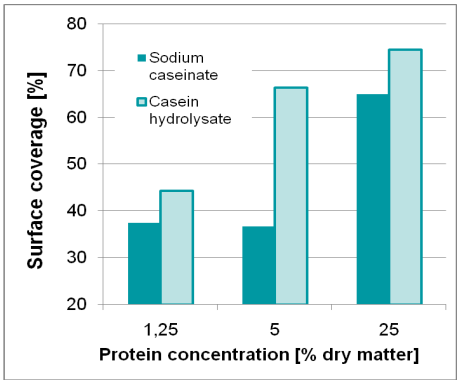

Figure 2: Surface coverage with protein in spray-dried micro particles with varying protein content and protein source as determined by XPS

CONCLUSIONS

In conclusion, a new experimental setup for the analysis of the dynamic surface tension in a time interval relevant for very fast processes during food manufacturing has been established. The results of the present study show significant differences in the surface-activity of caseinate and hydrolysed casein in an extremely short time-interval relevant for surface occupation after processes like atomisation during spray-drying. These results are confirmed by XPS analysis of the surface composition of spray-dried particles. It is concluded that molecular weight profile plays an important role for the surface activity of milk proteins, but other factors like surface hydrophobicity, hydrodynamic radius, number of ionisable groups and state of aggregation also need to be considered.

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REFERENCES

- Elversson, J. & Millqvist-Fureby, A. (2006). *In situ coating - An approach for particle modification and encapsulation of proteins during spray-drying.* International Journal of Pharmaceutics, 323, 52-63.
- Ward, A. F. H. & Tordai, L. (1946). *Time dependence of boundary tensions of solutions.* Journal of Chemistry and Physics, 14, 453-461.
- Liu et al. (2007) *Dissolution and enzymatic hydrolysis of casein micelles studied by dynamic light scattering.* Front. Chem. Eng. China, 1, 123-127.