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Influence of internal water phase gelation on the shear- and osmotic sensitivity of W/O/W-type double emulsions

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ABSTRACT

It has already been hypothesized and in some cases proven that gelation of the internal water droplets of W/O/W-type double emulsions might allow the application of a higher shear in the second emulsification step while maintaining a high internal water content. In this contribution, thermal denaturation of a concentrated whey protein isolate solution, which is used as the internal water phase, was investigated. Low-resolution NMR T_2-relaxometry measurements (using a CPMG-sequence) clearly showed that this thermal treatment effectively gelled the internal water phase. Using this approach, double emulsion droplets with a small average diameter (D_{43} of about 5 μm) and narrow particle size distribution were produced while a high internal water content was maintained. Moreover, our results indicated that gelation could not prevent osmotic shrinking of the double emulsion droplets upon dilution in hypertonic solution. However, gelation of the internal water phase clearly reduced the degree of osmotic swelling of the double emulsion droplets upon hypotonic dilution. However, this effect is probably due to droplet-globule coalescence occurring at lower internal water volume increases in case the internal water phase is gelled.

1. Introduction

Using water-in-oil-in-water (W/O/W)-type double emulsions, it is possible to produce functional (Berendsen, Güell, & Ferrando, 2015; Frank et al., 2012; Giroux et al., 2013; Jiménez-Colmenero, 2013) and fat reduced (Cofrades, Antoniou, Solas, Herrero, & Jiménez-Colmenero, 2013; Jiménez-Colmenero, 2013) oil-in-water (O/W)-type food emulsions because a part of the oil phase in the O/W-emulsion is replaced by water, which may contain functional ingredients.

Usually, the preparation of W/O/W-type double emulsions consists of a two-step procedure (Garti & Bisperik, 1998). In the first step, a W/O-emulsion is produced at high shear while in the second step, a double W/O/W-emulsion is produced at lower shear to avoid the disruption of the internal water droplets. Hence, double emulsion droplets are usually quite large and the particle size distribution is broad, because of the low shear in the second emulsification step (Opperman, Renssen, Schuch, Stieger, & Scholten, 2015). Interestingly, the amount of water that is retained after the second emulsification step appears to be directly dependent on the final double emulsion droplet size rather than the used emulsification device (Schuch, Wrenger, & Schuchmann, 2013).

It has already been hypothesized and in some cases proven that gelation of the internal water droplets might allow the application of a higher shear in the second emulsification step while maintaining a high internal water content (Iancu, Chevalie, Popa, & Hamaide, 2009; Opperman et al., 2015; Perez-Moral, Watt, & Wilde, 2014; Surh, Vladisavljević, Mun, & McClements, 2007). Hence, gelation of the internal water droplets might enable the production of double emulsion droplets with a sufficient amount of enclosed water as well as a small average diameter and narrow particle size distribution. This implicates that double emulsions can be produced which are more stable, for example against flocculation and creaming (Ivanov, Danov, & Kralchevsky, 1999; McClements, 1999).

Gelation can be achieved using a wide array of ingredients and preparation procedures. Whereas a reversible gel can be formed using starch (Iancu et al., 2009) or gelatin (Opperman et al., 2015), irreversible gels can be formed using alginate in combination with Ca^{2+}-ions (Perez-Moral et al., 2014; Paques, van der Linden, van

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Rijn, & Sagis, 2013) or thermal denaturation of a whey protein isolate (WPI)-solution (Opperman et al., 2015; Sağlam, Venema, de Vries, Sagis, & van der Linden, 2011; Surh et al., 2007). In this work, the latter method has been preferred, since high protein foods are considered to be a potential candidate for body-weight control and treatment of obesity (Sağlam et al., 2011). Furthermore, several studies emphasized the importance of proteins in the diets of the elderly (Campbell, Trappe, Wolfe, & Evans, 2001; Evans, 2004; Kurpad & Vaz, 2000).

Gelation of the internal water phase of a W/O/W-emulsion using thermal denaturation of a WPI-solution has already been described by other researchers. In the research reported by Surh et al. (2007), the water-in-oil (W/O)-emulsions under consideration were all equally stable in the second emulsification step, which may have been due to the high concentration of low-HLB emulsifier used. In contrast, Opperman et al. (2015) observed a higher retention of internal water when a WPI-gel was used as the internal phase. However, the double emulsion droplets produced in the latter work were quite large (diameter of about 70 μm). Moreover, in both publications, a real proof of the internal water phase gelation was not provided. In this research work, double emulsion droplets with a small average diameter and narrow particle size distribution were produced. The enclosed water volume fraction of these double emulsion samples was determined using low resolution pulsed field gradient (PFG)-NMR diffusometry (Vermeir, Balcaen, Sabatino, Dewettinck, & Van der Meeren, 2014), whereas low resolution NMR T_2-relaxometry was used to prove that the internal water phase in the W/O/W- or W/O-emulsion was indeed gelled (Colsenet, Mariette, & Cambert, 2005).

As the osmotic balance between the internal and external water phase is important to control the rheology and morphology as well as the release of encapsulated ingredients by droplet-globule coalescence (Delample, Da Silva, & Leal-Calderon, 2014; Iqbal, Baloch, Hameed, & McClements, 2013; Leal-Calderon, Homer, Goh, & Lundin, 2012; Mezzenga, Folmer, & Hughes, 2004), the osmotic behavior of the produced W/O/W-emulsions was also examined. Whereas water can still migrate throughout the gel network, gelation might render the internal phase more resistive to expansion or contraction. As shown by Colsenet et al. (2005), the addition of whey proteins to a water phase decreases the self diffusion coefficient of the water molecules due to the combination of hydration and obstruction effects of the proteins. Hereby, the reduction of the water diffusion coefficient was bigger in case a gel was formed and the divergence between solution and gel increased with increasing protein concentration.

2. Materials and methods

2.1. Materials

The lipophilic emulsifier polyglycerol polyricinoleate (PGPR 4150; min. 75% n-glycerols with n = 2, 3 and 4; max. 10% m-glycerols with m ≥ 7) and the hydrophilic emulsifier sodium caseinate (5.5% moisture; 96% protein on dry matter) were kindly provided by Palsgaard A/S (Denmark) and Armor Protéines (Saint Brice en Cogles, France), respectively. Sunflower oil was acquired from the local supermarket, while whey protein isolate was acquired from Davisco (BiPRO, Davisco, Le Sueur Food Ingredient Company, USA). The 0.1 M KCl (VWR Chemicals: BDH Prolabo, Leuven, Belgium) solution used in both the internal and external water phase contained 0.02 wt% of the anti-microbial agent NaN_3 (Sigma–Aldrich, Steinheim, Germany). KCl was added to both aqueous phases in order to reduce Ostwald ripening effects due to the high Laplace pressure of the internal water droplets which in turn is related to their small size and thus high curvature (Mezzenga et al. 2004).

2.2. Emulsion preparation

2.2.1. Preparation of the internal water phases (W_1)

The internal water phase consisted of 0.1 M KCl dissolved in deionized water containing 0.02 wt% NaN_3 and 5 or 10 wt% WPI. To induce gelation of these water phases, the solutions were placed in a water bath of 80 °C for 1 h. At this temperature, the water phase is expected to turn into a gel due to thermal denaturation and aggregation of WPI (Puyol, Pérez, & Horne, 2001).

2.2.2. W_1/O-emulsions preparation

The W_1/O-emulsion containing 5 wt% WPI in the internal water phase was prepared in duplicate; the double emulsions prepared using these primary emulsions are denoted with (1) and (2) hereafter. The oil phase consisted of sunflower oil containing 5 wt% PGPR. An Ultra-Turrax (type S50N-G45F, IKA®-Werke, Germany) at 5200 rpm was used to prepare the W_1/O-emulsions (50:50, w/w) at 60 °C. The water phase was added gradually while stirring after which stirring was continued to obtain the final W_1/O-emulsion. The obtained primary emulsion was split into two equal volumes: one sample was used as such in the preparation of a double emulsion while the other part was heated in a water bath at 80 °C for 1 h to gel the internal water droplets.

2.2.3. $W_1/O/W_2$ emulsions preparation

The external water phase (W_2) was mixed at room temperature with freshly prepared W_1/O-emulsion in a 50:50 (w/w) ratio with an Ultra-Turrax S25KV-25G (IKA®-Werke, Germany) at 6500 rpm for 1 min. This provided a macroscopically homogeneous but coarse double emulsion (premix). Hereby, the W_2-phase differed from the W_1-phase in the presence of 2 wt% of sodium caseinate and the absence of WPI. Afterwards, the premix was processed using a microfluidizer (type M110S, Microfluidics) at 140 bar (driving air pressure of 1 bar) while avoiding creaming by swirling the emulsion. The emulsion was cooled during homogenization by a heat exchanger that was immersed in a water bath of 25 °C. After 1, 2, 3 and 4 passes, samples were taken.

2.3. Low resolution NMR

NMR measurements were performed at 5 °C on a benchtop Maran Ultra spectrometer (Oxford Instruments, UK) operating at a frequency of 23.4 MHz. The samples of about 2.5 g were filled in 18 mm outer diameter glass NMR-tubes (Oxford Instruments, UK) and their exact mass was carefully noted.

The free self-diffusion coefficients of the used water phases (D) were measured using the DSD script (Oxford Instruments, UK) varying the duration (δ) in ten steps between 0.05 and 2.75 ms while keeping the gradient strength (g) and the diffusion delay (Δ) constant at 0.14 T/m and 200 ms, respectively. A standard STE-sequence was used to obtain the data after which following relation can be used to obtain D:

$$I(\delta, \Delta, g) = I_0 * \exp\left(- D * q^2 * \left(\Delta - \frac{\delta}{3} \right) \right)$$

Whereby

$$q = \gamma * g * \delta$$

I(δ,Δ,g) are the echo intensities in the presence of gradient pulses of length δ while I_0 is the echo intensity in the absence of gradient pulses. γ is the gyromagnetic ratio (2.675×10^8 s^{-1} T^{-1}).