New insights into the study of the destabilization of oil-in-water emulsions with dextran sulfate provided by the use of light scattering methods

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ABSTRACT

Emulsions are non-thermodynamically-stable systems. Being able to characterize their evolution upon time without disturbing them would be of great interest. Mechanisms of destabilization: depletion and bridging flocculation were reproduced by using dextran sulfate respectively with Tween 20 and whey-protein-stabilized oil-in-water emulsions. Two light scattering methods were combined: Multiple Light Scattering, MLS, specially adapted to characterize turbid systems (Turbiscan®) and Multi-Speckle Diffusing Wave Spectroscopy, MS-DWS (Rheolaser™). The Tween 20-stabilized emulsion showed a very stable-versus-time elasticity index (EI) measured by MS-DWS up to 24 h. On the contrary, the whey-protein-stabilized emulsions showed a large variation of EI that decreased continuously during 10 h and dropped to zero suddenly. On the basis of the physico—chemical interaction knowledge and the MLS profile evolution versus time, a variation of the destabilization kinetics depending on the droplet network stabilization but also on the interactions between droplets and the surface of the recipient was proposed. It was confirmed by the modification of the destabilization kinetics when changing the solid surface tension of the recipient.

1. Introduction

The knowledge of the destabilization mechanisms of oil-in-water emulsions is of particular interest for food emulsion conservation. Indeed such systems made up of a mixture of non-miscible fluids are thermodynamically unstable and the droplets may coalesce (Dickinson, 1992). Surface-active substances are usually used to stabilize the system. Due to their amphiphilic properties they adsorb at the interface, decrease interfacial tension and prevent coalescence (Dickinson, 1999). Moreover, several kinetic phenomena can occur during the emulsion's shelf life. Creaming is the gravity-driven movement of emulsion droplets. It leads to the formation of a cream layer at the top of the emulsion. According to Stokes' law based on the assumptions of laminar flow, spherical droplets, homogeneous material, smooth surface and absence of interference between droplets, the creaming rate mainly depends on the difference in density between the droplets and the bulk solution, the viscosity of the continuous phase and the particle radius (Dickinson, Goller, & Wedlockb, 1993; Robins, 2000).

The creaming can be slowed down by increasing the viscosity of the continuous phase through the addition of a thickening agent such as polysaccharides. The droplets are trapped in a three-dimensional network of entangled polymers. Nevertheless, when a non-adsorbing polymer is added into a moderately-concentrated emulsion, it may be excluded from the space between droplets depending on its hydrodynamic volume (McClements, 2000). Owing to the osmotic pressure, it may induce droplet aggregation by a depletion-flocculation phenomenon. Flocs of larger sizes are formed which cream faster. However, if the flocculation rate is higher than the creaming rate, droplet aggregates will form a weak particle network that is able to resist to gravitational force and then impede the creaming process. The system becomes rather stable (Damodaran, 2005). Another flocculation mechanism can occur depending on the nature and the concentration of the biopolymer added in the continuous phase. When the biopolymer is able to

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adsorb on the oil-droplet surface, depending on its concentration, individual polymers may interact with several droplets leading to a polymer bridge between droplets. This phenomenon is called bridging-flocculation (Jourdain, Leser, Schmitt, Michel, & Dickinson, 2008; McClements, 2009; Evans, Ratcliffe, & Williams, 2013). Flocculation may delay the destabilization time of the emulsion. In both flocculation mechanisms — depletion or bridging — a rearrangement of the droplets in the network occurs with time. Single or aggregated droplets tend to cream; the network formed during flocculation contracts itself and induces a phase separation with the formation of a serum layer (Blijdenstein, Van Winden, Van Vliet, van der Linden, & van Aken, 2004).

The study of emulsion structure was mainly based on experimental data obtained with droplet size distribution measurements, bulk shear rheology and ultrasonic measurements, microscopic observation and light scattering methods (McClements, 2007). In 2008, Corredig and Alexander reviewed recent applications of diffusing wave spectroscopy (DWS), a light scattering technique, to the study of oil-in-water food emulsions. This technique is non-invasive, non-disruptive and is able to study samples under realistic, non-diluted conditions. Indeed, DWS follows the temporal intensity fluctuation of a scattered light interference image (speckle). Based on the diffusive process, this fluctuation is related to the dynamics of the scattering particles and can be characterized by the intensity autocorrelation function in relation with time (Weitz & Pine, 1993). DWS is, then, able to provide quantitative information on local droplet motion in highly turbid media. The mean square displacement (MSD), corresponding to the mobility of a scatterer around its average position due to Brownian motion, is then measured.

Corredig and Alexander (2008) dated the first studies of oil-in-water emulsions using DWS at the very beginning of the 2000's. Two research groups proposed to use DWS for the monitoring of particle growth in oil-in-water emulsions with proteins (Hemar & Horne, 1999) and for the characterization of droplet aggregation in emulsions stabilized by polysaccharides (ten Grotenhuis, Paques, & van Aken, 2000; Hemar et al., 2003) without disturbance or need for dilution. Blijdenstein et al. observed that DWS results on oil-in-water emulsion depended on the flocculation velocity (Blijdenstein, Hendriks, van der Linden, van Vliet, & van Aken, 2003). By comparing DWS results of bridging- and depletion-flocculated β-lactoglobulin-stabilized emulsions Blijdenstein, van der Linden, van Vliet, and van Aken (2004); Blijdenstein, van Vliet, van der Linden, and van Aken (2003) showed differences between their elastic moduli (G′) calculated from MSD. However, that single rheological parameter was difficult to interpret without any information about the emulsion compositions.

With time, bridging- or depletion-flocculated emulsions evolve and undergo creaming because of gravity-induced droplet network compression. Turbidity measurements allowed showing that a flocculated emulsion had a delay time before creaming (Blijdenstein, Van Winden et al., 2004). Structural changes at colloidal scale may precede the macroscopic creaming. MS-DWS could therefore be interesting to follow local changes before macroscopic creaming. Moreover it could be of interest to record the DWS signal over time to see if any information could be extracted to compare bridging- and depletion-flocculated emulsions. However, the backscattering DWS signal results from the backscattering of a laser light by droplets of a concentrated emulsion in the vicinity of the surface. As such, its evolution with time, represented by MSD, depends on the ballistic motion due to gravity at large scale and to the local Brownian motion of droplets. Therefore, the motion perturbations at the cell's surface would largely contribute to the result of the measurement. It was demonstrated that oil droplets may adhere to a solid surface depending on the surfactant used to stabilize the emulsion and on

the surface properties during the flow of the emulsion (Dresselhuis, Stuart, van Aken, Schipper, & de Hoog, 2008). A thin layer can form at the contact with the solid surface. DWS has already been used to study film formation on solid surface (Giraud et al., 2009). One can wonder if interactions of oil droplets or specific components of the emulsion with the glass surface would slow down droplet motion and impact the signal in DWS obtained with a backscattering measurement.

The aim of this work was to confront informations on the destabilization mechanisms of emulsion provided by MultiSpeckle Diffusing Wave Spectroscopy to those provided by current light scattering methods. A special focus was made on the impact of the surface properties of the glass cell on the measured signal.

For this purpose we used a ready-to-use patented DWS instrument: Rheolaser™ (MultiSpeckle Diffusing Wave Spectroscopy-MS-DWS - Brunel, 2010). Rheolaser™ follows the temporal fluctuation of intensity of scattered light on a limited volume of turbid system, such as emulsion, during time. It provides information on the dynamics of the scattering particles, related to their diffusion coefficient and depending on the environnement. The results were interpreted in regard to the measurements of backscattering/transmission intensity of an incident laser light along the height of an optical glass tube using Turbiscan® (Mengual, Meunier, & Cayre, 1999). The backscattering profiles provided by Turbiscan® gave qualitative information on the distribution of the oil droplets and can be followed with time.

In this study, oil-in-water emulsions stabilized either by charged species (whey protein) or by uncharged species (Tween 20) were prepared. The flocculation was induced by the addition of dextran sulfate. Dextran sulfate may interact with charged proteins according to the controlled presence of electrolyte in the emulsion. But it may not interact with Tween 20.

2. Materials and methods

2.1. Materials

2.1.1. Raw materials

Powdered native whey protein concentrate (WPC), Prolacta 80, was supplied by Lactalis ingredients (Bourgbarre, France). The manufacturer's analyses indicated 80.0% (w/w of dry matter) of proteins and 4.0% (w/w of dry matter) of ash. Moisture of 7.1 wt% was determined through weighing and drying procedure. The whey proteins were mainly beta-lactoglobulin and alpha-lactalbumin.

Dextran sulfate (DS) sodium salt from *Leuconostoc* spp. (MW around 500,000 Da) was obtained from Sigma–Aldrich Co. (St Louis, USA). It contained approximately 95% of 1, 6-linked D-anhydroglucose units. The remaining units are 1, 3-linked and account for the branches. Dextran sulfate contained approximately 17% of sulfur which was equivalent to approximately 2.3 sulfate groups per glycosyl residue. Moisture of 4.7 wt% was determined through weighing and drying procedure. The intrinsic viscosity of this sample of dextran sulfate prepared in aqueous solvent with 0.28 wt % of NaCl was found to be equal to 2.2 ± 0.2 dL g^{-1}. This result was in accordance with data reported by Demetriades and McClements (1999).

Sodium chloride, Tween 20 and potassium sorbate were purchased from VWR (Radnor, USA).

The rapeseed oil from Lesieur (Fleur de colza), Rain Clear® liquid from Unelko Co. and French salad dressing were purchased from local retailers. The French salad dressing was composed of 25% of sunflower oil and contained xanthan gum and the mean droplet diameter was 35 ± 0.5 μm. Even if the detailed composition is not well defined, such a system is interesting for comparison with the model emulsions. Indeed, xanthan gum, with an intrinsic viscosity