The Diffusion and Coalescence Time Analyzer (DCTA): A novel experimental setup for investigating instability phenomena in double emulsions

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ABSTRACT

Double emulsions are of great interest for the encapsulation of e.g. bioactive substances, which is why they have constantly been in the focus of investigations during the last decade. Coalescence and diffusion phenomena lead to a decrease in encapsulation efficiency and cause an uncontrolled release of encapsulated molecules. In the present study, an innovative experimental setup for investigating these phenomena in double emulsions was developed. This setup was named *Diffusion and Coalescence Time Analyzer* (DCTA). It allows investigating the most crucial physical instabilities in double emulsions in one single experimental setup. First results obtained by varying the formulation which is known to influence the stability of double emulsions showed that the coalescence times can be related to the emulsion's structure and interfacial composition. The combination of the emulsifiers whey protein isolate (WPI) and polyglycerine-polyricinoleate (PGPR) shows a higher stability against coalescence than the use of only PGPR. With this model system, it was shown that the diffusion process of inner droplet molecules to the outer continuous phase can be quantified using the DCTA.

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1. Introduction

Water in oil in water ($W_1/O/W_2$) double emulsions consist of an inner water in oil (W_1/O) emulsion which is in turn dispersed in an outer aqueous phase (W_2). They were first described by Seifriz in 1923 (Seifriz, 1923). Due to their multicomponent structure, double emulsions possess high potential for the encapsulation and controlled release of e.g. active substances (Appelqvist, Golding, Vreeker, & Zuidam, 2007; Garti, 1997; McClements, 2015). Furthermore, in the food industry, double emulsions are discussed as systems enabling fat reduction without a change in sensorial properties (Lobato-Calleros, Rodriguez, Sandoval-Castilla, Vernon-Carter, & Varez-Ramirez, 2006; Lobato-Calleros et al., 2008).

In spite of their high potential for industrial application, the implementation in food products currently remains challenging due to the high thermodynamic instability of these systems

(Dickinson, 2011; Pays, Giermanska-Kahn, Pouligny, Bibette, & Leal-Calderon, 2002). Apart from physical instabilities such as droplet coalescence, Ostwald ripening, sedimentation or flocculation which are typical for single emulsions, further instabilities can occur in double emulsions. The coalescence between the inner water droplets and the outer water phase as well as the diffusion of water molecules from the inner to the outer water phase are of special interest as they lead to undesirable release of inner water and with this reduced encapsulation efficiency. The encapsulation efficiency EE describes the ratio by mass between the inner water phase after a specific time and the initial value for double emulsion production (Schuch, Köhler, & Schuchmann, 2012). Thus, the focus of this article is on the investigation of the physical instability mechanisms which can finally lead to the loss of the typical double emulsion structure (Ficheux, Bonakdar, Leal-Calderon, & Bibette, 1998; Pays et al., 2002). Besides the mentioned diffusion process further phenomena can occur that lead to the change in double emulsions structure. For example the diffusion of water molecules from the outer into the inner water phase. This process is osmotically driven and can be used to tune the inner microstructure of double emulsions (Mezzenga, Folmer, & Hughes, 2004). In addition, the rheological properties of double emulsion systems can be adjusted by a targeted diffusion of water from the outer through the inner water phase which is induced by pressure

differences. In this case, the principle idea is a fast concentration of gelling agents in the outer water phase based on the diffusion of outer water into the inner water phase (Delample, Da Silva, & Leal-Calderon, 2014). Regarding the application of double emulsions as encapsulation system, diffusion can also cause an uncontrolled loss of the encapsulated substances (Garti, 1997; McClements, 2015).

Previous experiments showed that the stability against coalescence of inner water droplets with the outer aqueous phase is mainly affected by the emulsion structure and the stabilizing agents used in the outer water phase. Schuch, Leal, and Schuchmann (2014) reported that the coalescence process takes place during the second emulsification step as well as in the first 20 min after the preparation of the double emulsion. The possibility to adjust the EE depending on emulsion structure by second step processing is reported by Schuch, Wrenger, and Schuchmann (2014) and Oppermann, Renssen, Schuch, Stieger, and Scholten (2015): The authors show that EE increases with an increasing W_1/O-droplet diameter. Therefore, low shear rates are recommended to disperse the W_1/O-emulsion in the W_2-phase in order to reach high EE (Garti & Bisperink, 1998; Schuch, Wrenger, et al., 2014; van der Graaf, Schroen, & Boom, 2005). Beside a suitable process, high amounts of stabilizing agents have to be used to reduce the loss of inner droplets by coalescence to the double emulsion's continuous phase. The presence of two interfaces (W_1/O and O/W_2) requires the use of at least two surfactants: a lipophilic one to stabilize the inner emulsion and a hydrophilic one to stabilize the outer emulsion. These surfactants are expected to adsorb at the respective interface and prevent droplet-droplet (W_1–W_1 or O–O) coalescence. However, the surfactants can adsorb at both interfaces and interact with each other. These interactions affect the interfacial properties and thus can influence the stability of double emulsions. For example, Kanouni, Rosano, and Naouli (2002) report that the use of a strong surface active emulsifier in the outer water phase can displace the lipophilic emulsifier at the W_1/O interface. The authors assume that this can eventually lead to a break of the double emulsion and therefore recommend the use of an efficient combination of high HLB surfactants. Not only the combination of emulsifiers itself but also the order of addition of those emulsifiers can influence the stability of the double emulsion and the interfacial properties. The emulsifiers compete in different ways at the interface which depends on the order of addition and is reflected in double emulsion structure. Another example is reported by Garti and Aserin (1996): a combination of bovine serum albumin (BSA) and sorbitan monooleate (Span 80) can form a viscoelastic gel film at the inner W/O interface due to a polymer-surfactant complex building. In Addition, the same combination of polymeric and monomeric emulsifier will form a protective colloid at the outer O/W_2 interface. Due to these interfacial properties, stable double emulsions regarding diffusion and thermodynamical instabilities can be prepared.

The second instability phenomenon leading to the loss of the inner structure comprises the diffusion of water molecules through the oily membrane to the outer continuous phase. This diffusion is caused by different capillary pressures. For a constant interfacial tension, the capillary pressure increases by decreasing the droplet size. Thus, the droplet size distribution in emulsion systems leads to pressure differences between droplets of different sizes. To balance these pressure differences, water molecules of smaller droplets diffuse into larger droplets. In the case of double emulsions, the pressure difference involving the inner water droplets and the outer water phase induces the diffusion between the two water phases.

Adding osmotic active substances to the inner water droplets is recommended to balance the pressure differences between the outer and the inner water phase (Jiao, Rhodes, & Burgess, 2002; Mezzenga et al., 2004; Rosano, Gandolfo, & Hidrot, 1998). However,

to calculate the needed amount of osmotic active substance, the droplet diameter of the inner water droplets has to be known before the emulsification process takes place. Another difficulty in calculating the total amount of the osmotic active substance is that the inner droplet diameter is distributed around a mean value. Furthermore, the osmotic active substance used for balancing the pressure difference might interact with other stabilizing agents (Márquez, Medrano, Panizzolo, & Wagner, 2010). In summary, each of the before mentioned interactions can alter the interfacial properties and can lead to a change in emulsion structure. Consequently, a good understanding of occurring interactions between emulsion ingredients is necessary to choose an efficient combination of stabilizing agents in double emulsions (Dickinson, 2011).

Up to know the investigation of the interactions between surfactants in double emulsions remains challenging. In most of the cases, the measurement techniques used to investigate those interactions cannot give any information about the type of water loss (diffusion or coalescence). For example, when using differential scanning calorimetry (DSC) to characterize the EE, only absolute values of the amount of inner water are determined (Schuch et al., 2012). The same problem occurs by using the nuclear magnetic resonance method described by Bernewitz, Dalitz, Köhler, Schuchmann, and Guthausen (2013). Using imaging or marker based techniques involve further disadvantages: the added dyes or markers often interact with the stabilizing agents and impair the stability of the double emulsion (Schuch, Tonay, Köhler, & Schuchmann, 2014). Thus, in order to gain a better understanding of the influence of formulation, it is necessary to develop further measurement devices to characterize instability mechanisms occurring in double emulsions.

In general, the coalescence process can be described in four steps (Hartland, 1967a, 1967b, 1967c): the first step comprises the contact between the two phases (e.g. droplet and interface). In the second step, the contact between those phases will cause the interfacial film to drain. When a critical film thickness is reached, the film will rupture in the third step. Finally, the droplet will fully or partially merge with the bulk phase in the last and fourth step. A large number of parameters, like geometric relations, interfacial properties and phenomena can affect this process. Due to the fact that the interfacial properties strongly depend on the applied stabilizing agents, only a short overview about the main effects will be given in the following section. Further information is summarized by Dickinson and Stainsby (1988). Since the droplets are always in contact with the other interface in the present investigation, the focus of this study lies on the influence on film drainage and consequent rupture (Step 2 and 3). For example, the Gibbs–Marangoni effect has a stabilizing impact on the film drainage. Here, the drainage of the fluid between the two interfaces, leads to the removal of surface-active compounds in the region of contact. A lower concentration of these compounds causes a decrease in surface tension in this region which leads to surface tension gradients along the interfaces. Due to this gradient, there will be a backflow of material into the contact region, which is called the Marangoni flow. This dynamic stabilization requires fast relaxation processes at the interface which are typical for emulsifiers with small molecular weights and can be characterized by the dilatational interfacial viscosity (Tan, Jiang, Liau, Grano, & Horn, 2009; Wantke & Fruhner, 2001). For larger molecules as for example proteins, the interfacial shear viscosity and the dilatational elasticity seem to have a greater influence on the coalescence phenomena. For example Dickinson, Murray, and Stainsby (1988) show a positive correlation between the interfacial shear viscosity and the stability against coalescence. With an increase in shear viscosity, mechanical strength of the interface increases which results in better stability.