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Formation of nanoemulsions in stirred media mills

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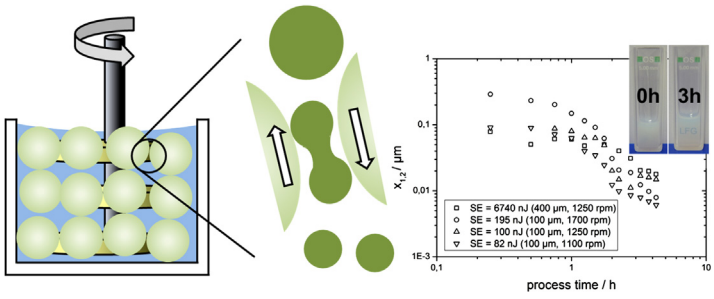
HIGHLIGHTS

- Stirred media mills are feasible devices to produce nanoemulsions ($x_{1,2} < 10$ nm).
- Emulsions of nominal oil mass fractions up to 20 wt% can be obtained.
- Influence of fundamental process parameters studied.
- Smallest product droplets are obtained while stressing below the melting point of the oil.
- The process is promising for emulsification of loaded oil phases too.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkane–Tween85–water-systems have been used as model emulsion systems to demonstrate the feasibility of emulsification in stirred media mills. The influence of fundamental process parameters, i.e. emulsion formulation (oil mass fraction and oil-to-emulsifier mass ratio), stress conditions (grinding bead size and stirrer tip speed), process time and especially temperature on the emulsion droplet size and size distribution has been studied for this approach. By lowering the process temperature below the solidification temperature of the oil phase, coalescence and ripening can be significantly reduced. Smallest product droplets with $x_{1,2} < 10$ nm thus are obtained even for nominal oil mass fractions up to 20 wt% in the hexadecane–Tween85–water system. The feasibility of the process proposed to produce nanoscale emulsions using oil phases loaded with compounds such as pigments and other fillers is demonstrated.

1. Introduction

Emulsions, i.e. colloidal systems composed of a continuous and a dispersed liquid represent a substantial part of products of the pharmaceutical and food industry (Binks, 1998; Schubert, 2010; Schuchmann and Danner, 2004; Walstra, 1993). In recent years an increasing use of emulsion-based delivery systems for bioactive substances involving small particle sizes (< 100 nm) is notable (McClements, 2012). Moreover, a lot of commodities used in personal care or cosmetics applications consist of emulsions. Besides these applications, emulsion-based systems have been applied to produce particles by precipitation processes as well as to assemble colloidal aggregates (see e.g. Lobaz et al., 2012; Winkelmann et al., 2013). Apart some cases of spontaneous emulsification or the formation of microemulsions, in general energy has to be introduced into the system to initiate the droplet breakup. The difference between 'nanoemulsions' and microemulsions was outlined in a recent paper by McClements (2012): whereas both types of emulsions may exhibit droplet sizes in

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the range below 100 nm, the thermodynamically stable microemulsions are formed by self-assembly: the process is either spontaneous or only a small activation barrier has to be overcome, i.e. slight agitation may lead to emulsification. In contrast, nanoemulsions are thermodynamically metastable, the emulsification process is not spontaneous and the droplet-breakup process needs application of external shear forces and a high energy input. The newly formed interfacial area needs to be stabilized by surface active compounds (emulsifiers) or particles (Kaiser et al., 2009; Köhler et al., 2010; Pickering, 1907; Stang and Schubert, 1998) in order to gain kinetic stability by preventing flocculation and decreasing the interfacial energy of the system and thus preventing coalescence of the droplets. Moreover, kinetic stability is superior for narrow droplet size distributions leading to a delay of destabilization processes such as Ostwald ripening, creaming or sedimentation.

Different devices for emulsification have been proposed so far. For low-viscous emulsions, devices using nozzles for the generation of defined flow conditions such as high pressure homogenizers, membranes, orifices or porous media (packed bed mixers) are frequently applied as well as methods exploiting cavitation phenomena. In the case of highly viscous dispersed phases rotor–stator devices are frequently used (Aguilar et al., 2004; Baumann et al., 2012; Christov et al., 2002; Feigl et al., 2003; Hövekamp, 2002; Kobayashi et al., 2003, 2005; Köhler et al., 2007; Köhler and Schuchmann, 2012; Mason et al., 2006; Nakashima et al., 1992; Tesch et al., 2002; Wolf et al., 2012). Moreover, phase inversion temperature (PIT) methods have been applied successfully to produce nanoscale emulsions (Bilbao-Sáinz et al., 2010; Shinoda and Arai, 1964; Tadros et al., 2004).

Within this account we show that stable water-n-alkane–Tween85 nanoemulsions can be produced by an alternative and scalable process applying stirred media mills. The stressing conditions in stirred media mills can be described by stress energy *SE* and stress number *SN*; the mass specific energy E_m is given by the product SE × SN (Kwade, 2003). According to Kwade (1999) SE is proportional to the energy that may be transferred upon collision of two grinding beads. The maximum value is given by the kinetic energy of one grinding bead, as described by the following equation:

$$SE_{max} \propto d_{GM}^3 v_{tip}^2 \rho_{GM} \quad (1)$$

d_{GM} is diameter of grinding media, v_{tip} is stirrer tip speed, and ρ_{GM} is grinding bead density.

The stress number *SN*, defined by the following equation, describes the total number of grinding bead collisions within a stirred media mill:

$$SN \propto \frac{\varphi(1-\varepsilon)}{(1-\varphi(1-\varepsilon))c_v} \frac{nt}{d_{GM}^2} \quad (2)$$

φ is volume fraction of grinding beads in the grinding chamber, $(1-\varepsilon)$ is packing density, c_v is concentration of product suspension, n is stirrer speed, t is process time, and d_{GM} is diameter of grinding media.

The possibility to produce nanoparticles in stirred media mills was shown by Stenger et al. (2005). Whereas the apparent grinding limit results from the interplay between breakage and agglomeration of broken fragments, the true grinding limit refers to the smallest achievable particle size of solid particles (Knieke et al., 2009, 2011). The motion of milling beads induces numerous stressing events upon the disperse particles which are seen to be essential for producing nanoparticles. Oxides with particle diameters as small as 10 nm have thus been obtained (Knieke et al., 2011). Recently, Schmidt et al. (2012) have shown that stirred media mills can be used to produce polymer particles below 5 μm. The transfer of results for solid particles to liquid droplets is straightforward since stressing of the disperse phase and the stabilization of the formed fine particles should follow similar rules, whereas the fracture of solid particles and the break-up of liquid droplets are distinctly different.

As will be outlined in this paper, remarkably, the shear and strain rates that may be realized in stirred media mills suffice for the production of nanoemulsions. The influence of process parameters such as grinding media size, stirrer tip speed, process temperature, i.e. emulsification of the liquid oil vs. 'grinding' of the solid oil phase and system composition on the emulsification result is discussed for hexadecane–Tween85–water systems. To minimize restrictions due to the emulsifier content (c.f. coalescence phenomena because of lack of emulsifier available in the system) high emulsifier to oil phase ratios have been applied.

2. Materials and methods

2.1. Materials

n-hexadecane (95%, for synthesis, Alfa Aesar) and n-dodecane (> 99%, Sigma Aldrich) have been used as oil phase without further purification. Tween 85 (Sigma Aldrich), a polyoxyethylene (20) sorbitan oleate, has been applied as the emulsifier. The feasibility of loading the oil phase with an organic substance was demonstrated for pyrene (> 98%, Alfa Aesar). The deionized water used for emulsification was supplied by a Millipore Simplicity 185 device.

2.2. Experimental setup

Emulsification experiments have been performed using a laboratory stirred media mill PE075 (Netzsch). Oil and emulsifier mass fractions between 1wt% and 20 wt% have been applied within this study. The stress intensity SE (see Eq. (1)) has been varied by changing the grinding bead size d_{GM} and stirrer speed v_{tip}. As grinding media Yttria-stabilized ZrO_2 grinding beads (YSZ, Tosoh) of a density of 6050 kg/m^3 and diameters of 100 μm and 400 μm, respectively, have been used. Approximately 1500 g of grinding beads have been filled into the grinding chamber (total volume 650 ml). First, the emulsifier was dissolved in the water, and then the oil phase was added. A raw emulsion (droplet sizes in the order of magnitude of several 10–100 μm) was prepared in a beaker by using a magnetic stirrer and subsequently transferred to the grinding chamber. The raw emulsion is quite unstable, i.e. it separates within minutes: low agitation does not suffice for the formation of stable emulsions. The stirrer tip speed v_{tip} has been varied between approximately 3.3 m/s and 6.1 m/s, i.e. agitator speeds between 1000 rpm and 1700 rpm have been applied. The process temperature was set between 10 °C and 32 °C. It was kept constant over the process time using a thermostat device RC6 (Lauda).

2.3. Characterization

Emulsion droplet size distributions have been obtained by dynamic light scattering measurements using an Ultrafine Particle Analyzer UPA device (Microtrac). All size measurements have been performed at room temperature.

Dynamic and static interfacial tensions have been determined using the bubble pressure tensiometer BP100 (Krüss) and the droplet contour analysis device DSA100 (Krüss), respectively.