Performance of microfluidics in the preparation of O/W nanoemulsions containing green solvents

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Abstract

Emulsions are colloidal thermodynamically unstable dispersions in which a liquid is dispersed in a continuous liquid phase in the form of droplets. Emulsions are used as end or intermediate products in many fields, like cosmetics, food industry, pharmacy, medicine, polymers, catalysts and agrochemistry.

The role of solvents in agrochemical industry is becoming increasingly more important. More than 25% of all pesticides contain high concentrations of organic solvents, which represent a fire hazard, may be toxic and contribute to atmospheric volatile compound (VOC) emissions [1]. Thus, many of the classical solvents are being gradually replaced by the so-called 'green' solvents, such as fatty acid dymethilamides and D-Limonene. Fatty acid dimethylamides (FAD) are solvents that fulfil the requirements to be considered green solvents and may find application in agrochemicals. D-Limonene, a naturally occurring hydrocarbon, is a cyclic monoterpene, which is commonly found in the rinds of citrus fruits such as grapefruit, lemon, lime, and in particular, oranges. Limonene exhibits good biodegradability, hence it may be proposed as an interesting alternative to organic solvents. α-pinene is also a renewable solvent, which may be obtained from pine resins or distillation. These solvents can meet the ever-increasing safety and environmental demands of the 21st Century.

The most common emulsification methods are based on mechanical energy input to the system by an external source. As a rule, emulsions are prepared in two steps; the aim of the first (primary homogenization) is to create droplets of dispersed phase such that a coarse emulsion is formed. The goal of the second step is to reduce the size of preexisting droplets, which usually involves the use of a different homogenizer. Rotor-stator homogenizers, colloid mills, membranes, ultrasonic probes, high pressure- valve homogenizers and microfluidizers are currently used to prepare emulsions [2].

The droplet size distribution (DSD) of the emulsion depends on the emulsification method used. DSD is perhaps the most important factor in determining properties like consistency, rheology or shelf life stability of emulsions. On the whole, emulsions with smaller droplet sizes result in greater physical stability. It is well documented that DSD plays an important role in the retention of volatile and surface oil content of powders during microencapsulation by spray drying [3]. It is interesting to highlight the increasing importance of emulsions with submicron droplet diameter and a narrow DSD in many fields like food, pharmaceutical and cosmetic industries [4].

Typically emulsions with a high percentage of submicron droplets are produced either by using a high-pressure valve homogenizer (HPvH) or a Microfluidizer. An HPvH consists of a piston pump and a narrow gap, where a valve reaches an operating pressure of up to 150 MPa. Droplet break-up occurs within the region of the valve gap and in the jet after the gap. A Microfluidizer operates at a similar maximum pressure, generated with a piston pump, and droplet break-up occurs from high turbulence and shear created by the collision of two impinging jets oriented 180^{o} to each other. Forcing the flow stream by high pressure through microchannels toward an impingement area creates a tremendous shearing action, which can result in exceptionally fine emulsions. Some studies have pointed out that the microfluidization technique is capable to obtain emulsions with lower mean droplet diameters and narrower DSDs than traditional emulsifying devices [5].

The goal of this work was to investigate:

a) The influence of emulsification method on the DSD and physical stability of O/W eco-friendly emulsions formulated with a mixture of green solvents (α-pinene and N,N-Dimethyl decan-1-amide (DMA-10)) as oil phase. Four different emulsification methods based on two rotor-stator devices (Ultraturrax T50 and Silverson L5M) and two high-pressure homogenizers (Avestin Emulsiflex C5 and Microfluidizer M110P) have been used.
b) The influence of emulsification pressure, from 35 to 172 MPa, on the rheological properties, DSD and physical stability of O/W eco-friendly emulsions containing a mixture of d-limonene and DMA-10 as oil phase.

A glycereth-17 cocoate (Levenol C201®) has been used as emulsifier. Polyoxyethylene glycerol esters derived from cocoa oil (Levenol) are non-ionic surfactants which fulfil the environmental and toxicological requirements to be used as emulsifiers in order to design eco-friendly products. DSD measurements were perfomed by laser diffraction with a Mastersizer X (Malvern). Multiple light scattering (MLS) scans were carried out with a Turbiscan Lab-expert (Formulaction) for about 75-100 days at 25 ºC, which provided early information on the destabilization kinetics and the main mechanism involved. This technique is able to detect instability problems long before the naked-eye. The rheological measurements were carried out with a CS Haake-MARS rheometer (Thermo), using a sandblasted Z20 coaxial cylinder geometry to avoid slip-effects.

Figure 1 illustrates the influence of emulsification method on the values of Sauter mean diameter ($d_{3,2}$), volumetric mean diameter ($d_{4,3}$) and span for some representative emulsions processed with four different methods. All methods allowed submicron emulsions to be prepared, but the Microfluidizer M110P and the Avestin EmulsiFlex C5 achieved the lowest Sauter diameters (about 280 nm in both cases). However, the Microfluidizer M110P provided emulsions with lower values of volumetric diameter and span (related to polidispersity) than Avestin Emulsiflex C5. The latter gave rise to an emulsion showing some recoalescence. This phenomenon is currently associated to an excess of mechanical energy input during the emulsification process [4]. In addition, MLS measurements showed that emulsions processed with the Microfluidizer exhibited a higher stability against creaming. This could be ascribed to the lower mean diameters and polidispersity achieved with the Microfluidics.

Interestingly, the influence of the homogenization pressure on the DSD in these emulsions was not significant, conversely to rheological properties, which were substantially influenced by the homogenization pressure. All emulsions studied exhibited shear thinning behaviour, which fitted the Cross model. A decrease of emulsification pressure yielded an increase of the zero shear viscosity. This could be related to a flocculation process, which subsequently triggered a coalescence process, as demonstrated by Laser Diffraction.

References

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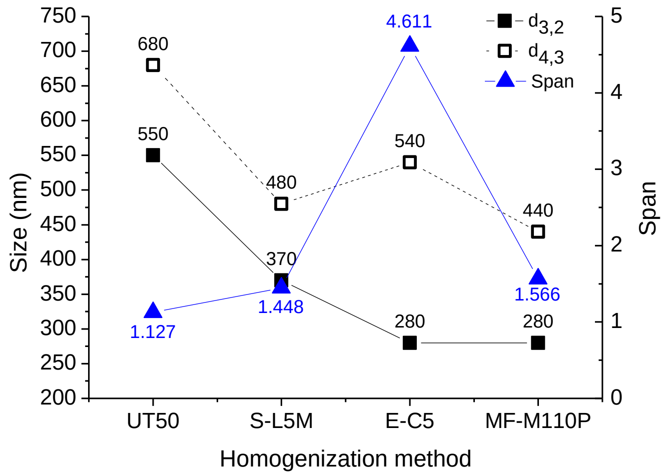

Figure 1. Sauter diameter, volumetric diameter and span for emulsions processed with different emulsification methods.