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Comparison of homogenization processes for the development of green O/W emulsions formulated with *N*,*N*-dimethyldecanamide

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ABSTRACT

The target of this work was to compare the yield of three homogenization processes (two different rotor–stator devices and a high-pressure valve homogenizer) for the development of O(green solvent)/W emulsions containing an eco-friendly emulsifier. Rheology, laser diffraction, optical microscopy and multiple light scattering were the main techniques used to assess the efficiency of homogenization methods. First the best values of the processing variables were obtained for each homogenizer and secondly a comparison of properties of emulsions prepared with these optimum processing conditions was carried out. The results obtained revealed that the more stable emulsions were prepared with an Ultraturrax T25.

Introduction

Researchers are engaged in exploring new green solvents for different applications, due to the current trends in green chemistry and green engineering, and to replace the traditional organic solvents. Nowadays, the development of commercial formulations containing these compounds has risen. A promising alternative for their application is the formulation of new oil-in-water (O/W) emulsions in which the green solvent remains distributed as small droplets in a continuous phase formed by water. O/W emulsions are utilized in several industrial and medical applications for a variety of reasons. For example, in the agrochemical industry, pesticides need solvents in order to dissolve solid actives. The main advantage of these emulsions is that they are aqueous based formulations, thus making easy their application, and reducing their environmental impact.

Dimethylamides of fatty acids (FAD) are biosolvents that meet the requirements to be considered as green solvents, which have been developed to be mainly used in agrochemicals [1]. In fact, an emulsifiable concentrate (EC) formulated with an FAD as solvent has been recently patented to be used as an herbicide [2]. *N*,*N*-dimethyldecanamide is considered a safe green solvent according to the Environmental Protection Agency. This biosolvent has been used as the oil phase, in combination with α-pinene or D-limonene, for the development of ecological oil-in-water (O/W) emulsions [3–5].

Many agrochemicals formulations include surfactants as emulsifying agents [6]. An eco-friendly surfactant, namely a polyoxyethylene glycerol ester obtained from coconut oil (Levenol C-201™), fulfils the toxicological and environmental demands to be used as an emulsifying agent in the development of eco-friendly products [7]. This non-ionic surfactant also possesses an eco-label (DID: 2133). In fact, it has been included in formulations of commercial detergents and personal care products in various patents [8,9]. In addition, the wetting and interfacial properties at the air/water and α-pinene/water interface of this surfactant have been recently reported [10–12].

Emulsions consist of two immiscible liquids where one of the liquids is dispersed in the other as small spherical droplets. Emulsions are, however, thermodynamically unstable systems and quickly tend to undergo phase separation. The most common emulsification method consists of providing mechanical energy from an external source, creating and breaking disperse phase droplets [13]. Modern emulsions can be produced by specially designed devices including high-pressure, ultrasonic, rotor–stator, and membrane systems [14,15]. Numerous studies concerning high-energy emulsification techniques are available in the literature [16,17]. The most commonly used high-energy emulsification techniques are rotor–stator and high-pressure systems. Many emulsion properties such as droplet size distribution and physical stability depend on the homogenization method used [18].

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Rotor–stator homogenizers consist of a high-speed rotor enclosed in a stator, with the gap between them ranging from 100 to 3000 μm [15]. As the rotor rotates, it generates a lower pressure to draw the liquid in and out of the assembly, thereby resulting in circulation and emulsification [19,20]. The high shear (shear rate ranges from 20,000 to 100,000 s^{-1}) attained in these devices is the main driving force which can reduce the size of the dispersed droplets, but elongational stress, turbulence and cavitation are also factors to be taken into consideration [21]. The emulsion droplet size is determined by the homogenization intensity (power) and the residence time that emulsion droplets stay in the shearing field. Other parameters that might affect the performance of rotor/stator homogenization are the viscosity of the two liquids, surfactant, rotor/stator design, volume size, and volume ratio of the two phases [22]. Depending on the design of the rotor and stator they can be classified into three main geometric groups: colloidal mills, toothed devices and radial discharge impellers [23]. Toothed devices such as Ultraturrax have an open structure and a good pumping capacity. Another rotor–stator design is the radial discharge impeller, such as the Silverson device, with a rotor that is a radial impeller that rotates inside a stationary stator perforated with differently sized holes. There is a set of interchangeable stators enabling the device to be used for different applications. A high-pressure valve homogenizer consists of a piston pump and a narrow gap, where a valve reaches a high operating pressure. Droplet break-up occurs within the region of the valve gap and in the jet after the gap.

The aim of this research was to assess the performance of a standard rotor/stator, a rotor/stator equipped with a fine emulsor-screen and a high-pressure valve homogenizer in the preparation of slightly concentrated lab-scale emulsions. The efficiency of the different homogenization processes was assessed by analysing the droplet size distribution, the microstructure, the shear flow properties and the physical stability of emulsions. The emulsions were formulated using *N*,*N*-dimethyldecanamide as oil phase and a polyoxyethylene glycerol fatty acid ester as emulsifier. These emulsions may find applications related to the design of biotechnological complex systems with different uses, such as matrices for agrochemical products or emulsion-based encapsulation and delivery systems.

Materials and methods

Materials

N,*N*-dimethyldecanamide (Agnique AMD-10™) was kindly provided by BASF. The emulsifier used was a nonionic surfactant derived from coconut oil. Namely, a polyoxyethylene glycerol fatty acid ester, glycereth-17 cocoate (HLB: 13), received as a gift from KAO, was selected. Its trade name is Levenol C-201™. A blend of polydimethylsiloxane and modified starch (Rhodia) was used as defoaming agent. Deionised water was used for the preparation of all emulsions. Taking into account previous results, the composition of the O/W emulsions prepared consisted of 3 wt.% Levenol C-201™ as emulsifier, 0.1 wt.% antifoam emulsion and 30 wt.% solvent ($\phi_v = 0.33$) [24].

Emulsification processes

The emulsions were prepared using the following homogenization processes (Table 1):

1. Some emulsions were prepared with a standard rotor/stator mechanical homogenizer Ultraturrax T25 (dispersion element KV09-93). First of all a semi-batch step (rotational speed: 6500 rpm) was used, in which the oil phase was slowly added for 60 s to the aqueous surfactant solution. Subsequently, a batchwise procedure was used with an operation time of a further 60 s. The sample amount per batch was 60 g. Homogenization speed was the processing variable studied and ranged from 9500 rpm to 24,000 rpm. This experimental set-up will be denoted below as T-25.
2. Other emulsions were prepared with a rotor/stator mechanical homogenizer Silverson L5M equipped with a fine emulsor-screen (L5M). Once again the first step followed a semi-batch protocol (oil added for 60 s while the rotational speed was 6500 rpm). The rotational speed for the batchwise step was increased to 8000 rpm and the homogenization time was the process variable selected in this case. This ranged from 10 s to 300 s. The sample amount per batch was 250 g. The acronym L5 M will stand for this homogenization set-up.
3. High-pressure valve homogenization was conducted with an Avestin Emulsiflex C5 homogenizer (HPvH). First of all, a primary emulsion was prepared with the Ultraturrax T25 operating at 17,500 rpm in the batchwise stage. Final emulsions were prepared at either 50 MPa or 150 MPa with 1 or 2 passes. This process will be termed below (HPvH).

Temperature was fixed at 15 °C for all processing methods by a thermostatic-cryostat bath.

Emulsion droplet size analysis

The mean droplet diameter of emulsions was calculated from the droplet size distribution (DSD) using a laser diffraction instrument (Mastersizer X, Malvern Instruments). The results

Table 1
Emulsification methods and processing variables used for the preparation of studied emulsions.

	Step 1	Step 2	
Rotor–stator homogenization (Ultraturrax T25)	Semi-batch processing (60 s, 6500 rpm, 15 °C)	Batchwise processing (60s, 15 °C)	9500 rpm 13,500 rpm 17,500 rpm 21,500 rpm 24,000 rpm
Rotor–stator homogenization with fine emulsor screen technology (Silverson L5M)	Semi-batch processing (60 s, 6500 rpm, 15 °C)	Batchwise processing (8000 rpm, 15 °C)	10 s 30 s 60 s 120 s 300 s
High pressure valve homogenization (Avestin emulsiflex C5)	Semi-batch processing (60 s, 6500 rpm, 15 °C) [Ultraturrax T25]	50 MPa 150 MPa	1 Pass 2 Passes 1 Pass 2 Passes

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