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Physical stability of *N*,*N*-dimethyldecanamide/α-pinene-in-water emulsions as influenced by surfactant concentration

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ABSTRACT

In recent years, interest in submicron emulsions has increased due to their high stability and potential applications in the encapsulation and release of active ingredients in many industrial fields, such as the food industry, pharmaceuticals or agrochemicals. Furthermore, the social demand for eco-friendly solutions to replace hazardous solvents in many dispersion formulations has steadily risen. In this study, the influence of surfactant concentration on the formation and physical stability of submicron oil-in-water emulsions using a high-pressure dual-channel homogenizer (microfluidizer) has been investigated. The formulation involved the use of a blend of two green solvents (*N*,*N*-dimethyldecanamide and α-pinene) as dispersed phase and a nonionic polyoxyethylene glycerol ester derived from coconut oil as emulsifier (Levenol® C-201), which enjoys a European eco-label. Therefore, these emulsions may find applications as matrices for agrochemicals. Physical stability and rheological properties of the emulsions studied showed an important dependence on the eco-friendly surfactant concentration. The lowest surfactant concentration (1 wt%) yielded the onset of a creaming process after a short aging time and was not enough to avoid recoalescence during emulsification. On the other hand, the higher surfactant concentrations (4–5 wt%) resulted in depletion flocculation, which in turn triggered emulsion destabilization by coalescence. The optimum physical stability was exhibited by emulsions containing intermediate surfactant concentrations (2–3 wt%) since coalescence was hardly significant and the onset of a weak creaming destabilization process was substantially delayed.

1. Introduction

Nowadays, the use of agrochemical products is associated with environmental pollution and the presence of toxic residues in the final products. An alternative is the use of low-risk pesticides and herbicides based on green solvents. These green solvents must be obtained from renewable materials and exhibit high biodegradability [1]. Emulsifiable concentrates (ECs) are among the most widely used agrochemical systems due to their versatility. However, in recent years there has been a strong trend to replace them with concentrated oil-in-water emulsions (EWs). The partial removal of oil results in less phytotoxicity and skin irritation to the customer. In addition, the sizes of droplets can be adjusted to an optimum distribution, which is important to increase biological efficacy [2]. Agrochemical products with small droplets and narrow droplet size distributions have been shown to improve biological activity [2].

Fatty acid dimethylamides are among the green solvents that can find applications in agrochemicals [3]. *N*,*N*-dimethyldecanamide (AMD-10™) is considered a safe biosolvent, according to the Environmental Protection Agency. Another biosolvent considered to be an interesting alternative to traditional solvents is α-pinene. It represents the major constituent of turpentine oils from the wood of most conifers and from leaf oils obtained from some herbs, such as juniper, rosemary or parsley [4]. For these reasons, the formulation of blends of these solvents in oil-in-water (O/W) concentrated emulsions has been studied in this work.

The selection of the emulsifier used to stabilize the emulsion is crucial since it must fulfill several requirements; in addition to being able to stabilize an emulsion exhibiting suitable physicochemical properties, the surfactant must be biodegradable and non-hazardous for agricultural applications.

Polyoxyethylene glycerol esters derived from coconut oil are non-ionic surfactants obtained from a renewable source. Their excellent wetting, interfacial and emulsifying properties are well documented [5–7]. These surfactants are fully innocuous to human

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skin and hair and their properties are appropriate for the design of eco-friendly products [8–11]. Interestingly, these surfactants fulfill the environmental and toxicological requirements permitting their use as eco-label materials in Europe. One of these green surfactants, Levenol® C-201 (glycereth-17 cocoate) possesses an eco-label (DID list: 2133).

One of the main challenges in the development of these O/W emulsions is the control of their physical stability in order to achieve an adequate shelf-life. Once emulsions are prepared, it is vital to detect at an early stage the onset of any destabilization process to shorten aging tests. In addition, determining the destabilization mechanisms provides outstanding feedback on formulation and processing variables [12]. Droplet size distributions (DSD) are perhaps the most important factor in determining properties like biological efficacy, rheology or shelf-life stability of emulsions [13]. On the whole, emulsions with smaller droplets and narrower DSDs result in longer stability. Double channel homogenization using a Microfluidizer (Microfluidics) is the methodology of choice if fluid-like emulsions with submicron mean diameters and narrow droplet size distributions are the targets, since they can reach extremely high shear rates [14].

Surfactant concentration is one of the key variables when dealing with emulsion formulation; hence it must be carefully controlled. On the one hand, a minimum emulsifier concentration is required to fully cover the available interfacial area created during the emulsification process. On the other hand, an excess of surfactant in solution will lead to the formation of a great number of micelles. It is well known that non-adsorbed surfactant micelles may induce the flocculation of the emulsion droplets due to a depletion mechanism [15,16]. This phenomenon, known as depletion flocculation, in turn, may trigger irreversible destabilization processes such as creaming and/or coalescence [17,18].

The main objective of this work was to study the influence of surfactant concentration on the physical stability of slightly concentrated O/W emulsions formulated with these eco-friendly solvents. A further goal was to prepare stable fine emulsions developed by double channel microfluidization, which may be find applications as matrices for the incorporation of active agrochemical ingredients. These emulsions not only contain an eco-friendly surfactant but also a blend of two green solvents, which contributes to the increasing demand for the development of more sustainable chemical dispersions.

2. Materials and methods

2.1. Materials

According to the composition of emulsions previously studied, 30 wt% O/W emulsions formulated with a non-ionic surfactant (glycereth-17 cocoate) at different concentrations were prepared using a mixture of green solvents, as dispersed phase. *N*,*N*-dimethyl decanamide (AMD-10™) and α-pinene were utilized with a 75/25 mass ratio [19].

Agnique AMD-10™ (density: 0.88 g/mL at 25 °C) was kindly provided by BASF. α-Pinene (density: 0.84 g/mL at 25 °C) was supplied by Sigma Chemical Company. The emulsifier used was a non-ionic surfactant derived from coconut oil. Namely, a polyoxyethylene glycerol fatty acid ester, glycereth-17 cocoate, received as a gift from KAO, was selected on account of its HLB number, 13. Its trade name is Levenol® C-201. The influence of Levenol® C-201 concentration on the stability and physicochemical properties of the emulsions was studied in the 1 to 5 wt% range.

2.2. Emulsification procedure

The continuous phases were prepared by dissolving Levenol® C-201 surfactant in ultrapure water cleaned using a Milli-Q water purification system. Emulsions were prepared in two steps. First of all, 250 g of a coarse emulsion was prepared using an Ultraturrax T50 rotor-stator homogenizer with a toothed S50-G45F dispersion unit working at 4000 rpm for 120 s. Oil phase was slowly added for 30 s to the continuous phase and the temperature was fixed at 20 °C using a semibatch set up assisted by a circulator to keep the temperature at the set point. Subsequently, secondary homogenization was carried out with a Microfluidizer (model M110P with an F12Y interaction chamber, Microfluidics, USA) at 15000 psi (103.42 MPa) in order to obtain lower droplet diameters and narrower droplet size distributions. Samples kept under storage at 20 °C.

2.3. Emulsion droplet size analysis

Size distributions of oil droplets were determined by laser diffraction using a Mastersizer X (Malvern, United Kingdom). All measurements were done three times for each emulsion 24 h after being prepared and results are reported as the mean and standard deviation. These measurements were carried out during 60 days of aging time to monitor the kinetics of emulsion destabilization by either coalescence or Ostwald ripening.

The mean droplet diameter was expressed as Sauter mean diameter ($D_{3,2}$) and volumetric mean diameter ($D_{4,3}$):

$$D_{3,2} = \frac{\sum_{i=1}^{N} n_i d^3{}_i}{\sum_{i=1}^{N} n_i d^2{}_i} \quad (1)$$

$$D_{4,3} = \frac{\sum_{i=1}^{N} n_i d^4{}_i}{\sum_{i=1}^{N} n_i d^3{}_i} \quad (2)$$

where d_i is the droplet diameter, N is the total number of droplets and n_i is the number of droplets having a diameter d_i.

To determine the distribution width of droplet sizes, "span" was used, calculating from the following formula:

$$span = \frac{D(v, 0.9) - D(v, 0.5)}{D(v, 0.1)} \quad (3)$$

Where D(v,0.9), D(v,0.5), D(v,0.1) are diameters at 90%, 50% and 10% of cumulative volume, respectively.

2.4. Physical stability

Multiple light scattering measurements with a Turbiscan Lab Expert (Formulaction, France) were used in order to complete the study on emulsion destabilization. Measurements were carried out until 40 days at 20 °C to determine the predominant mechanism of destabilization in each emulsion as well as the kinetics of the destabilization process.

The Turbiscan Stability Index (TSI) is a parameter that can be used to estimate the physical stability of dispersions like suspensions or emulsions. This parameter is a statistical factor and its value is obtained as the sum of all processes taking place in the studied probe. An increase in TSI value means that the overall physical stability of the dispersion under study decreases. TSI values were calculated using the equation [11]:

$TSI = \sum_j |scan_{ref}(h_j) - scan_i(h_j)|$ (4)where $scan_{ref}$ and $scan_i$ are the initial backscattering value and the backscattering value at a given time, respectively, h_j is a given height in the measuring cell and TSI is the sum of all the scan differences from the bottom to the top of the vial.