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Influence of the concentration of a polyoxyethylene glycerol ester on the physical stability of submicron emulsions

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ABSTRACT

The chemistry and technology of agrochemical products has undergone extensive changes over the last 20 years. The new formulations and ingredients should meet the needs of the agrochemical industry for products having greater safety to the user and much lower environmentally impact maintaining the same performance targets. A recent trend involves the use of the emulsion format for agrochemicals, which provides a more efficient performance than those conventionally used. Furthermore, the production of submicron stable emulsion is a key achievement especially for this product.

This study has been focused on the development of fine emulsions containing ecofriendly ingredients, such as surfactants and green solvents. It has been proven that the optimal surfactant concentration not only may lead to emulsions with submicron droplet sizes but also may prevent the typical destabilization process occurring in these formulations. In this particular case, it has been demonstrated that 3 wt% surfactant concentration is adequate for three reasons: (a) allowing the lowest droplet size to be achieved, (b) providing the sufficient viscosity to prevent creaming and (c) not being an excess of surfactant that leads to depletion flocculation.

1. Introduction

Emulsion science and technology has been used for many years to create a diverse range of commercial products, including pharmaceuticals, foods, agrochemicals, lubricants, personal care products, and cosmetics. Production of emulsion-based systems with specific physicochemical and functional properties often requires tight control over the particle size distribution (McClements, 2005). Type and concentration of emulsifier play an important role in the droplet size distribution (DSD).

The interest in submicron emulsions has increased in recent years due to their very small droplet size and high stability and their applications in many industrial fields such as personal care and cosmetics, health care, pharmaceuticals, and agrochemicals. (Schultz et al., 2004; Sonneville-Aubrun et al., 2004; Leal-Calderon et al., 2007; McClements, 2005; Tadros, 2009). These emulsions whose range in the DSD falls typically of 100–500 nm are also sometimes referred to as ultrafine emulsions (Nakajima, 1997), mini-emulsions (El-Aasser and Sudol, 2004) and nanoemulsions (Tang et al., 2013). In addition, submicron emulsions can be prepared by reasonable surfactant concentrations (less than 10%) that may fulfil the requirements of a bio-based society (Brökel et al., 2007).

There is a need to replace the traditional organic solvents by more environmentally favourable solvents (Anastas and Warner, 1998.) Consequently, the renewed interest in search of appropriate greener and alternative solvents to be used

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in emulsions has grown enormously (Sheldon, 2005). Fatty acid dimethylamides (FAD) are among green solvents that can find applications in agrochemicals (Hofer and Bigorra, 2007). N,N-dimethyldecanamide (DMA-10) is considered a safe biosolvent, according to the Environmental Protection Agency. Therefore, it is a great solvent for agrochemical use due to the lack of risk to the farmer. The fact of satisfying the needs of customers is the basic principle of the product design (Brökel et al., 2007).

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. D-Limonene exhibits good biodegradability, hence it may be proposed as an interesting alternative to organic solvents (Walter, 2010; Medvedovici et al., 2012). These solvents can meet the ever-increasing safety and environmental demands of the 21st Century.

Environmentally friendly surfactants have attracted significant interest recently. Polyoxyethylene glycerol esters derived from cocoa oil are non-ionic surfactants obtained from a renewable source which fulfil the environmental and toxicological requirements to be used as ecofriendly foaming and/or emulsifying agents, hence their consideration as green surfactants (Castán and González, 2003). Their use in detergents and personal care products is disclosed in several patents (Lutz, 2006; Denolle et al., 2011). Levenol C-201 was selected as emulsifier due to its great superficial and interfacial properties. Furthermore, α-pinene emulsions with Levenol C-201 showed better stability than emulsions containing its counterpart Levenol H&B (Trujillo-Cayado et al., 2014a, 2014b)

The main objective of this work was the study of the influence of the surfactant concentration (polyoxyethylene glycerol ester) on the physical stability of slightly concentrated O/W emulsions formulated with a mixture of green solvents (N,N-dimethyldecanamide and D-limonene). The optimum ratio of these solvents was previously studied by Santos et al. (2014). A further goal was to achieve stable fine emulsions, which may be used as matrices for incorporation of active agrochemical ingredients. According to a recent study (Santos et al., 2014), the same strategy was followed considering the combination of different techniques, which was proven to be a powerful tool to provide very interesting information at an early stage about the mechanisms of destabilization occurring in emulsions.

2. Materials and methods

2.1. Materials

N,N Dimethyl Decanamide (Agnique AMD-10™) was kindly provided by BASF. D-Limonene was supplied by Sigma Chemical Company. The emulsifier used was a nonionic surfactant derived from cocoa 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™. The safety data sheet provided by the supplier reports a value for oral toxicity (LD50) higher than 5000 mg/kg of animal in tests carried out with rats. It is interestingly to note that this value would be 3000 mg/kg for salt (Hollinger, 2005).

RD antifoam emulsion (DOW CORNING®) was used as antifoaming agent. This commercial product consists of an aqueous solution containing Polydimethyl siloxane (<10%w/w) and Dimethyl siloxane, hydroxyl-terminated (<10%w/w). Deionized water was used for the preparation of all emulsions.

2.2. Submicron emulsion development

Emulsions containing 0.1 wt% antifoam emulsion, a variable surfactant concentration and 30 wt% mixture of solvents (75 wt% AMD-10/25 wt% D-limonene) were prepared. The optimum ratio of solvents was previously studied by Santos, 2014. The surfactant concentrations studied were 1.5, 2, 2.5, 3, 3.5 and 4 wt%. These O/W emulsions were carried out using a rotor–stator homogenizer (Silverson L5M), equipped with a mesh screen at 6000 rpm during 60 s.

2.3. Droplet size distribution measurements

Size distribution of oil droplets was determined by laser diffraction using Mastersizer X (Malvern, Worcestershire, United Kingdom). All measurements were repeated 3 times with each emulsion. These measurements were carried out after 1, 3, 13, 21, 40 days aging time to analyze likely coalescence effects.

The mean droplet diameter was expressed as Sauter diameter ($D[3, 2]$) and volume mean diameter ($D[4, 3]$).

$$D[M, N] = \left[\frac{\int D^M n(D)dD}{\int D^N n(D)dD}\right]^{1/M-N} \quad (1)$$

2.4. Rheological measurements

Rheological experiments were conducted with a Haake MARS controlled-stress rheometer (Thermo-Scientific, Germany), equipped with a sand-blasted coaxial cylinder Z-20 (sample volume: 8.2 mL, $Re/Ri = 1.085$, $Ri = 1$ cm) to avoid slip effects. Flow curves were carried out from 0.05 Pa to 1 Pa at 20 °C. Flow curves were carried out after 1, 3, 13, 21 and 40 days to check the effect of aging time. All measurements were repeated 3 times with each emulsion. Samples were taken at about 2 cm from the upper part of the container. Sampling from the top part of the container in contact with air was avoided.

2.5. Multiple light scattering

Multiple light scattering measurements with a Turbiscan Lab Expert were used in order to study the destabilization of the emulsions. 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. Multiple light scattering is a sensitive and non-intrusive technique to monitor physical stability of emulsions (Allende et al., 2008; Camino et al., 2012) and more complex systems such as suspoemulsions (Santos et al., 2013).

Multiple light scattering measurements in the middle zone of the measuring cell also allowed the evolution of a mean droplet diameter with aging to be monitored.

2.6. Viscosity of the continuous phase

The viscosity of continuous phases solutions (from 2.14 wt% to 5.71 wt%) were measured with an Ubbelohde glass capillary viscometer. A volume of solution was pipetted into the capillary viscometer, which was equilibrated at 20 °C in a water bath for 30 min prior to measurements. All the measurements