Highly concentrated emulsified microemulsions as solvent-free plant protection formulations

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ABSTRACT

Effective plant protection agents are readily available and well implemented in industry. However, delivery to the plant and application on the leaf are processes that still need to be optimized. Up to now plant protection formulations represent either emulsion or suspension concentrates that often contain environmentally harmful organic solvents and/or adjuvants. Emulsified microemulsions are hierarchically organized systems comprising emulsion droplets that confine a water-in-oil microemulsion. In the present contribution we show that emulsified microemulsions prepared from environmentally friendly components can be loaded with the plant-protection agent Fenpropimorph® up to 48 wt.% without organic solvent. The emulsion itself is highly concentrated, containing 60 wt.% of dispersed phase, and can be readily diluted with water for spraying in farming applications. Small-angle X-ray measurements reveal the existence of a water-in-Fenpropimorph® microemulsion confined inside the emulsion droplets. Dynamic light scattering shows that the emulsions prepared are monomodal, comprising droplet radii in the hundred nanometer range.

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1. Introduction

To effectively fight plant diseases is the overall goal of any plant protection agent. In industry, efficient plant protection agents are currently available; however, delivery optimization in terms of application on the plant leaf is still challenging. The concentrated plant-protection formulation must be emulsified or diluted and sprayed by the farmer. The aerosol needs to adhere to the plant leaf surface and the plant protection agent must then penetrate the waxy leaf surface to become active. Up to now, common plant-protection formulations are emulsion concentrates (ECs) or suspension concentrates (SCs). ECs consist of a combination of surfactants and active ingredients to be emulsified by the farmer, whereas SCs are concentrated colloidal suspensions that only need to be diluted by the farmer. In the formulation of ECs or SCs, environmentally harmful organic solvents and/or adjuvants are often used. Any optimization in this area will help to save costs and will be beneficial for the environment. Herein, we present internally

self-assembled emulsions as delivery systems for the liquid, hydrophobic plant-protection agent Fenpropimorph®. The formulation is ready to use and simply needs to be diluted with water to prepare the desired concentration. The formulation can be loaded with up to 48 wt.% of plant-protection agent without the use of harmful organic solvents or adjuvants.

Internally self-assembled emulsions are hierarchically ordered systems that represent self-assembly in confinement. Nanostructures with a high internal interfacial area consisting of water and oil domains separated by an amphiphilic monolayer are confined to droplets of typically 100 nm radius. While the emulsion or dispersion is kinetically stabilized, the confined nanostructure is in the equilibrium state. According to the bulk-phase behavior of the primary emulsifier used, the confined structure thus changes reversibly as a function of temperature [1]. The internal nanostructure formed is an expression of the local curvature of the interfacial film H. Besides temperature, the addition of oil, co-surfactants or guest molecules can be used to tune the interfacial curvature and, hence, to modify the confined nanostructure in the desired way [2–4].

The production of internally self-assembled emulsions can be achieved by simply dispersing or emulsifying nanostructured bulk material in a continuous water phase [5] by using conventional techniques. It has proven useful to apply ultrasonication to low levels of dispersed nanostructured phase (up to 30 wt.%) and to a

Couette shear cell at high amounts of dispersed nanostructured phase (10 wt.% up to 70 wt.%) [6]. It is essential for the formation of internally self-assembled emulsions that the nanostructure to be confined be either oil-continuous or bicontinuous, since the resulting dispersion or emulsion is of the oil-in-water type. Primary emulsifiers that self assemble to build up these nanostructures have a critical packing parameter (cpp) > 1 [7]. To avoid diffusion of the primary emulsifier into the continuous water phase and hence destabilization of the internally self-assembled emulsion, the primary emulsifier must build up nanostructures that can be sufficiently swollen with water, but (above a certain level) phase-separate into a water–swollen nanostructured phase and a water-excess phase. Hydrophobic primary emulsifiers that fulfill these pre-conditions are surfactant-like lipids such as monoglycerides or Phytantriol® [8,9]. Both exhibit rich phase behavior in water, showing a variety of liquid–crystalline phases, such as inverse hexagonal H_2 and bicontinuous cubic phases of diamond $Pn3m$ and gyroid type $Ia3d$ and a fluid isotropic phase L_2. However, in view of large-scale applications, recent studies indicate that the purity of the applied hydrophobic primary emulsifier may play a crucial role since impurities can significantly alter the binary phase behavior in water [10].

To stabilize the internally self-assembled particles, amphiphilic polymers such as the high molecular weight tri-block copolymer Pluronic®F127, proteins or nanoparticles have been used [11–17]. The stabilizer must have sufficient solubility in water to be effective in oil-in-water type dispersions and emulsions. Note that in the case of Pluronic®F127 the amount of stabilizer was found to have a strong influence on the internal nanostructure and on the overall dispersed particle size, whereas for particle-stabilized dispersions no interaction with the internal structure could be observed [18].

We show that internally self-assembled emulsions can be loaded with the plant-protection agent Fenpropimorph® up to 48 wt.%. Preliminary greenhouse tests demonstrate that even an unoptimized emulsified microemulsion performed as well as the commercially available optimized formulation. We show how performance-enhancing adjuvants, such as the spreading enhancer Plurafac®LF120, can change the internal nanostructure and influence the stability of internally self-assembled emulsions.

2. Materials and methods

2.1. Materials

Phytantriol® (3,7,11,15-tetramethyl-1,2,3-hexadecanetriol) was purchased from DSM chemicals in technical grade. Pluronic® F127 (PEO_{99}–PPO_{67}–PEO_{99}) was donated by BASF SE (New Jersey, USA). Dimodan U® was purchased from Danisco A/S (Brabrand, Denmark).

Fenpropimorph® and Plurafac LF120® were donated by BASF SE (Limburgerhof, Germany).

All substances were obtained as technical grade, and were used without further purification. For the preparation of the internally self-assembled dispersions and emulsions, bi-distilled water was used, for the DLS measurements MilliQ water, and for the greenhouse experiments CIPAC standard water.

2.2. Preparation of internally self-assembled dispersions/emulsions

2.2.1. Parameters defining the composition

$$\delta = \frac{m_{\text{primary emulsifier}}}{m_{\text{oil}} + m_{\text{primary emulsifier}}}$$
$$\times 100 \quad \text{content of primary emulsifier in dispersed phase}$$

$$(1)$$

$$\phi_m = \frac{m_{\text{oil}} + m_{\text{primary emulsifier}}}{\sum_i m_i} \times 100 \quad \text{content of dispersed phase}$$

$$(2)$$

$$\beta = \frac{m_{\text{secondary emulsifier}}}{m_{\text{oil}} + m_{\text{primary emulsifier}}}$$
$$\times 100 \quad \text{ratio of secondary emulsifier to dispersed phase}$$

$$(3)$$

$$\lambda = \phi_m \left(1 - \frac{\delta}{100}\right) \quad \text{total load of oil} \quad (4)$$

Depending on the amount of dispersed phase, ϕ_m, two different methods for the preparation of internally self-assembled emulsions were used. In all cases, unless otherwise stated, stabilizer Pluronic®F127 was used as 20 wt.% stock solution. The stock solution was diluted with either bi-distilled or CIPAC standard water to the desired β values. Typically β-values of 8 or 10 were applied.

2.2.2. Ultrasonication – up to 30 wt.% of dispersed phase

Oil phase and primary emulsifier were weighed into a glass vessel and mixed to prevent the formation of a cubic phase. After homogenization, water and Pluronic® F127 stock solution were added. Unless otherwise stated, a total amount of 10 g dispersion/emulsion for each individual preparation was produced. The mixture was exposed to pulsed ultrasound using 0.5 s pulse and 1.5 s delay at 120 W for 20 min total exposure time without cooling (SY-LAB GmbH, Pukersdorf, Austria).

2.2.3. Couette shear cell – above 30 wt.% of dispersed phase

We have applied a laboratory-built shearing device [6] derived from a Couette shear cell with a fixed gap width of 100 μm. The shear rate was kept constant at 15,000 s^{-1}, while the shearing temperature was adjusted for each dispersion/emulsion prepared. To produce highly concentrated emulsions a premixed raw emulsion was poured into the top opening of the shearing device and sheared as fast as possible through the narrow gap between the rotor and the stator by applying mechanical pressure. Premixing of the raw emulsion was performed with a heated spatula; the dispersed phase and the continuous phase were prepared and thermostated separately at the shearing temperature, and were then mixed together just before shearing. According to the dimensions of the shearing device we could produce at least 10 mL of emulsion within a few seconds.

2.3. Small angle X-ray scattering

SAXS measurements were performed using a SAXSess camera (Anton Paar, Graz, Austria), which was connected to an X-ray generator (Phillips, PW 1730/10) operating at 40 kV and 50 mA with a sealed-tube Cu anode. A Göbel mirror was applied to convert the divergent polychromatic X-ray beam into a focused, line-shaped beam of monochromatic Cu Kα radiation (λ = 0.154 nm). The 2D scattering pattern was detected by a PI-SCX fused fiber optic taper CCD Camera from Princeton Instruments, a division of Roper Scientific Inc. (Trenton, NJ, USA) and integrated into the 1D scattering function $I(q)$. The CCD detector featured a 2084 × 2084 array with 24 × 24 μm^2 pixel size (chip size 50 × 50 mm^2) at a sample to detector distance of 311 mm. The CCD was operated at −30 °C and cooled with water at 10 °C to reduce the thermally generated charge. Cosmic-ray correction and background subtraction were performed on the 2D image prior to further data processing. No sample background was subtracted. The temperature of the capillary and the metallic sample holder were controlled by a Peltier element. Samples were equilibrated at 25 °C for 15 min prior to