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Influence of non-ionic surfactant type on the salt sensitivity of oregano oil-in-water emulsions

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ABSTRACT

During the last decade, there has been a growing interest for more "label-friendly" ingredients in food industry, as well as in pharmaceuticals, and cosmetics. Thus, a lot of research has been developed to the antimicrobial and/or antioxidant characteristics of essential oils. We, therefore, examined the influence of environmental stress conditions (i.e. salt addition and acidification) on the stability of oregano essential oil emulsions that were stabilized by either Tween 80 or Inutec SP1. Whereas Tween 80 is a non-ionic, food-grade ethoxylated sorbitan ester, Inutec SP1 is a biodegradable and renewable hydrophobically modified inulin. Whereas the emulsions prepared with Tween 80 exhibited phase separation (oiling off) at all salt concentrations studied, the emulsions stabilized with Inutec SP1 remained stable for several days; pH variation on the other hand exhibited no significant effect on the stability. Diffusion ordered spectroscopy measurements by nuclear magnetic resonance (DOSY NMR) as well as viscosity measurements suggested the dehydration of the polyoxyethylene (POE) head groups of Tween 80 upon NaCl addition. Measurements by a Quartz crystal microbalance with dissipation, on the other hand, presented no NaCl effect on the thickness of the adsorbed Tween 80 layer to a hydrophobic surface. Besides the effect of NaCl addition or pH variation, the influence of the ripening inhibitor concentration in the lipid phase and/or temperature variation on the Ostwald ripening levels were also investigated. Emulsions containing a 50:50 ratio of oregano essential oil to sunflower oil stored at 4 °C exhibited a significant reduction in Ostwald ripening rate. This study has implications for the development of essential oil emulsions to be used as antimicrobial agent when exposed to environmental stress conditions.

1. Introduction

Commercial marinades are widely used for quality enhancement to improve organoleptic as well as techno-functional properties of meats [1,2]. Most marinades are water based emulsions consisting of salt, organic acids, sugar, oil, spices, herbs, and food additives, such as antimicrobial and antioxidative agents [1–3]. Organic acids (lactic, acetic and citric acid) and salt (NaCl) are employed to enhance both flavour and microbiological quality of the immersed meat [4,5]. As food consumers prefer natural preservatives rather than synthetic ones, essential oils (EOs) are in a great demand. EOs are secondary metabolite compounds produced by aromatic plants and herbs [6–9]. They are a complex mixture of volatile and natural compounds that can have interesting features including antioxidant, antimicrobial, and antifungal properties [10–12]. Oregano is one of the EOs derived from Oregano herbs (mint family) containing a high amount of phenols, which are phytochemical compounds [11,13]. In this study, Origanum Compactum essential oil was selected due to its strong ability as an antimicrobial agent [3,11].

As these essential oils frequently have to be used in an aqueous environment, there is a need for colloidal delivery systems [14–18]. Nanoemulsions containing small oil droplets (< 200 nm) can be utilized as delivery systems for EOs [19]. Nanoemulsions are of particular interest because of their advantages over conventional emulsions such as a high physical stability, higher transparency, and increased bioavailability [11,20,21]. However, it is difficult to produce stable nanoemulsions of EOs due to the relatively large aqueous solubility of EOs, which makes them more prone to the Ostwald ripening (OR) phenomenon.

If oregano EOs emulsions are used in a marinade, it is crucial that they remain stable towards gravitational separation, flocculation, and coalescence during long-term storage in a stress environment. In this

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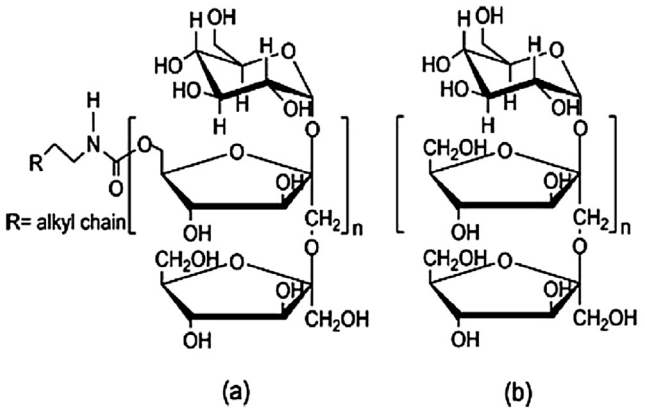

Fig. 1. Chemical structure of a) Inutec SP1 and b) native inulin [26].

respect, the selection of a suitable surfactant to formulate these emulsions plays an important role.

Non-ionic surfactants are not able to create stabilizing long-range electrostatic forces [22]. However, by generating short-range hydration/protrusion forces, they may prevent emulsion droplets from coming into direct contact with each other [23], and hence can suppress coalescence. In general, nonionic surfactants are resistant to flocculation by addition of salt [24]. The insensitivity of non-ionic surfactants to the presence of electrolytes is related to the fact that the dimensions of the non-ionic chains vary relatively little with electrolyte concentration [24]. Moreover, steric repulsion is fairly insensitive to pH. Thus, in this study Tween 80 (Polyoxyethylene (20) sorbitan monooleate) was originally selected as it has the advantages of being environmental friendly, commercially inexpensive, non-toxic and biocompatible [25].

As previous studies showed that nanoemulsions stabilized by Inutec SP1 are resistant to high salt concentrations [43–45], the latter was used as an alternative emulsifier. Inutec SP1 is a graft copolymer that is made by hydrophobic modificationof the polysaccharide inulin (Fig. 1) [26,27]. The latter is obtained from chicory roots and consists of a linear polyfructose chain with a glucose end [28]. Native inulin has 2–60 fructose units which is then fractioned to smaller molecules with lower molecular weight. Low viscosity and effective stability of emulsions in the presence of high electrolyte concentration are advantages of Inutec SP1 [27]. Tadros [29] designated two major advantages of Inutec SP1. First, it can be attached to the particle or droplet by multi-point attachment of the molecule to the interface. In addition, it has a high degree of hydration by its linear polyfructose chains, even in the presence of high electrolyte concentrations and high temperatures and hence has a high potential for steric stabilization.

The focus of our study was to establish the influence of stress conditions on the stability of oregano essential oil in water emulsions. In this research, also the factors that can reduce Ostwald ripening such as addition of a hydrophobic oil in the lipid phase and lowering of the storage temperature were investigated. The information obtained from this research can be used to formulate oil in water emulsions which remain stable within the challenging environmental conditions that may occur in a marinade.

2. Materials and methods

2.1. Materials

EO from oregano (Origanum Compactum) was obtained from Pranarom International (Belgium). The EO was used without further purification. Inutec® SP1 was generously provided by BENEO Orafti (Tienen, Belgium). Tween 80, Inulin from chicory, Polyethylene glycol-12,000, Sodium DL-Lactate solution in H_2O with a concentration of 50% (w/v) (St. Louis, MO, USA), Lactic Acid solution with a concentration of ≥85% (w/v) (Steinheim, Germany), ammonia solution (25%), 1-hexadecanethiol (> 95%), and sodium azide (≥99.5% were all purchased from Sigma-Aldrich Co. Hydrogen peroxide solution (30%) was provided by Merck (Merck, Darmstadt, Germany). High Oleic Sunflower Oil (HOSO) (Iodine value = 87; 82% C18:1) was obtained from Contined B.V. (Bennekom, The Netherlands). Sodium chloride, sodium acetate trihydrate, and ethanol (> 99%) were provided by VWR PROLABO Chemicals (Belgium). Deuterium oxide (heavy water, 99.8%) was purchased from Armar (Döttingen, Switzerland). Ultrapure water purified by a Milli-Q filtration system (0.22 μm) (Millipore Corp., Bedford, MA, USA) was used for the analyses and preparation of all aqueous solutions.

2.2. Stock emulsion preparation

Stock emulsions were prepared by mixing 5% w/w of an oil phase (containing Oregano EO and/or HOSO) and 95% w/w aqueous solution containing 0.5% w/v of surfactant. The mixture was pre-emulsified with a high speed stirrer (Ultra-Turrax, type S 50N – G 45 F, IKA®-Werke, Germany) for 2 min at 24,000 rpm. After pre-emulsification the mixture temperature was checked to be kept at 20 °C. The mixture was homogenized by passing 5 times through a Microfluidizer (M110-S, Microfluidics Corp., Newton, MA) at a pressure of 112 MPa to form a nanoemulsion. During microfluidization, the emulsion was cooled down by placing the heat exchanger coil into an ice water bath. The influence of HOSO concentration was examined by homogenizing a 5% w/w lipid phase which consisted of variable ratios of oregano EO and HOSO (oregano oil: HOSO = 100:0, 95:5, 90:10, 85:15, 80:20, 70:30, 50:50, 0:100% w/w) with 95% (w/w) aqueous phase.

In order to have a series of emulsions of the same particle size with different salt concentrations or pH, sodium lactate buffer solution at the desired pH (i.e. either 3, 4, or 5) and/or NaCl stock solution (30%w/v) were initially mixed and then the stock emulsion was diluted with the same volume of the prepared salt and buffer mixture. Hence, the final oil concentration of the emulsions became 2.5%w/w whereas the buffer concentration was 4 mM (irrespective of the pH). The blank samples were diluted in Milli-Q water with the same ratio containing 0.02% sodium azide. The pH of buffer and salt mixture solutions was checked to be kept constant and adjustments were performed with either sodium lactate or lactic acid (0.4 M). In the case of temperature effect investigation, the diluted colloidal dispersions were kept at 4, 20, and 40 °C.

2.3. Emulsion characterization

2.3.1. Stability evaluation

The creaming stability was evaluated by Lumifuge® 116 stability analyzer that applies a centrifugal force to the samples in order to accelerate the demixing process [30]. The resulting movement of the particles causes a variation of the transmission profile which is recorded by a charge-coupled device (CCD) line sensor. The prepared samples (0.4 ml) were placed into a polycarbonate cell and the measurements were performed at room temperature (20 °C) during centrifugation for 1 h at 3000 rpm which corresponds to 1147 × g. The creaming velocity was calculated by front tracking in the range of 95–113 mm (from the center of rotation), whereby a trigger value of 20% was selected.

Visual assessment of possible creaming, phase separation, and oiling off was also performed during storage in the gravitational field and in certain cases, digital photos were taken.

2.3.2. Particle size determination

The droplet size distribution of the samples was measured using either dynamic or static light scattering. The z-average mean particle diameter of the emulsion was measured using Photon Correlation Spectroscopy (Model 4700, Malvern Instruments, U.K.) at a scattering angle of 150° at 25 °C. The emulsion was diluted prior to analysis with