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Emulsification by high frequency ultrasound using piezoelectric transducer: Formation and stability of emulsifier free emulsion

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ABSTRACT

Emulsifier free emulsion was developed with a new patented technique for food and cosmetic applications. This emulsification process dispersed oil droplets in water without any emulsifier. Emulsions were prepared with different vegetable oil ratios 5%, 10% and 15% (v/v) using high frequency ultrasounds generated by piezoelectric ceramic transducer vibrating at 1.7 MHz. The emulsion was prepared with various emulsification times between 0 and 10 h. Oil droplets size was measured by laser granulometry. The pH variation was monitored; electrophoretic mobility and conductivity variation were measured using Zêtasizer equipment during emulsification process. The results revealed that oil droplets average size decreased significantly ($p < 0.05$) during the first 6 h of emulsification process and that from 160 to 1 μm for emulsions with 5%, 10% and from 400 to 29 μm for emulsion with 15% of initial oil ratio.

For all tested oil ratios, pH measurement showed significant decrease and negative electrophoretic mobility showed the accumulation of OH^- at oil/water interface leading to droplets stability in the emulsion. The conductivity of emulsions showed a decrease of the ions quantity in solution, which indicated formation of positive charge layer around OH^- structure. They constitute a double ionic layer around oil particles providing emulsion stability. This study showed a strong correlation between turbidity measurement and proportion of emulsified oil.

1. Introduction

Emulsions are generally prepared with surface active agents (surfactant) [1–3] or amphiphilic polymers [2] to reduce interfacial tension. Emulsion stability is due to adsorption of stabilizer at oil/water interface creating electrostatic repulsion [1] and steric repulsion for emulsions containing polymers [4]. When emulsifier is added, it may interact with the other formulations compounds creating new emulsion properties. Therefore, it becomes difficult to study the role of oil phase alone on emulsion properties. The fraction of emulsifier in materials will greatly influence the purification and performance of the products [5]. Emulsifier absence should expose essential features of oil droplets themselves [2].

In ultrasonic emulsification, the sound ranges used for food can be divided into high-frequency/low-energy ultrasounds and low-frequency/high-energy power ultrasounds [6].

High frequency ultrasounds are usually used as a nondestructive, rapid, easy-to-automate, and relatively inexpensive analytical technique for quality assurance and process control with particular reference to physicochemical properties, such as composition, structure, physical state and molecular properties of foods [6]. As well as being used as an analytical instrument in the laboratory, ultrasound can also be used for continuous monitoring of food properties on-line during processing [7].

High frequency ultrasounds go through solid or liquid media without affecting their structure and are used as diagnosis tools e.g. analysis and medical imaging [8]. HF ultrasounds were used in different applications, such as quality control of food, commercial cooking oils, bread and cereal products, bulk and emulsified fat based food products, food gels, aerated and frozen foods, improvement in mass transfer, food preservation, support of thermal treatments, texture improvement and food analysis [9,10].

These low energy ultrasounds have frequencies above 1 MHz at intensities below 1 W cm^{-2}. They have been used for non-destructive action on genetic improvement programs; it is also used for evaluating compositions of raw and fermented meat products and for evaluating composition of fish and poultry. On the other

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hand, high power (low frequency) ultrasounds induce mechanical, physical and chemical changes through cavitation, which induce many food processing operations such as extraction, emulsification and inactivation of food bacteria [11,12]. In ultrasound system, the droplet disruption is due to the physical shear force provided predominantly by the process of acoustic cavitation [13]. The use of low frequency ultrasound for emulsion formation is well established, mostly on an analytical laboratory scale [14]. Nano/microemulsions with the desirable droplet size can be easily generated from a variety of materials with ultrasound using only a fraction of the power of conventional mechanical devices [15]. Within ultrasound range, the power available varies inversely with the frequency and only powerful ultrasounds (16–100 kHz, and, to a lesser extent, 100 kHz–1 MHz) interact with matter, producing physical and chemical changes, essentially by cavitation phenomena [8] that is formation and subsequent collapse of micro-bubbles by pressure fluctuations of a simple sound wave causing extreme levels of highly localized turbulence "high pressure and high temperature" [11,16,17].

These ultrasounds (low frequency) use intensities higher than 1 W cm^{-2} and frequencies between 20 and 500 kHz, which are disruptive and induce effects on the physical, mechanical or chemical and biochemical properties of foods [9].

The impacts of ultrasound treatment on sunflower oil using two different ultrasound arrangements (titanium and Pyrex) were evaluated by Pingret et al. [18]. The study showed an increase of formed radicals in sonicated oils, as well as modifications of physicochemical parameters, particularly oils oxidation [18].

The aim of this work was to use high frequency ultrasounds and low energy emulsification to create a non-denaturing and non-destructive emulsification process avoiding chemical changes in emulsions without emulsifier. This study evaluated applicability of new emulsification process using high frequency ultrasounds for generation of emulsifier-free emulsions with different oil ratios from: 5%, 10% and 15% (v/v).

2. Materials and methods

2.1. Material

Distilled water and commercially available sunflower oil were used as aqueous and oil phases, respectively, for all prepared emulsions. Sunflower oil was used for emulsification and (vegetable oil, Lesieur) purchased from a local supermarket (Nancy, France). Aqueous solution pH was adjusted at 10.0 before emulsification process with 1 N NaOH solution. The NaOH was purchased from Fisher Scientific (France). The higher emulsified oil ratio was observed when an emulsion aqueous phase was adjusted at pH 10.0. Beattie and Djerdjev [19] produced emulsions with several emulsification steps and maintained a basic pH (pH = 9) throughout all step of emulsification process. After each step, NaOH was added to maintain a constant pH, allow a supply of OH^- and provide an electrostatic stabilization for emulsion. In our study, the pH was not maintained during the emulsification process, but initially adjusted to pH 10 and pH changes was followed during the emulsification process. All materials were used as received, without further purification.

A piezoelectric transducer was supplied by Hydro factory, Ltd. (Sarcelles, France). The volume of emulsion reactor was 6 l. The piezoelectric transducers were equipped with a piezoelectric ceramic with 20 mm diameter vibrating under electric field influence. The ultrasonic frequency was chosen as 1700 kHz. Operation voltage was 24 V and electric current intensity was between 0.82 and 0.90 A.

2.2. Preparation of oil droplet dispersions

Emulsion was generated according to Genialis patent (N149668A1). Ultrasonication dispersed oil droplets in water without any surfactant. Emulsification was made with piezoelectric ceramics vibrating at high frequency ultrasounds with maintained temperature at 25 °C.

Water and oil were placed in a thermostated reactor. For each liter, two transducers were added. Twelve piezoelectric transducers were placed at the bottom. Water and sunflower oil were exposed to emulsification process with high frequency ultrasounds during 10 h. Samples were taken every 2 h for analyses. Various sunflower oil ratios were tested: 5%, 10% and 15% (v/v) and emulsion volume was 6 l.

2.3. Size measurement

The mean distribution of oil globules was measured using a laser light scattering particle size analyzer with Mastersizer S (Malvern Instruments Ltd. UK) equipped with a He–Ne laser, with a beam of light of 360 nm, and wet sample analyzer that allowed emulsion measurements. The system was able of detecting particles in size ranging from 0.05 μm up to 900 μm. Measurements were carried out in ten replicates for each emulsion. Results were reported as typical globules size distribution in μm, the volume-weighted mean globule size $D(4,3)$:

$$D(4,3) = \sum n_i d_i^4 \Big/ \sum n_i d_i^3$$

where n_i was the number of particle i; d_i was the diameter of the particle i (μm). Oil globule size distribution was determined from the best fit between experimental measurements and prediction using the Mie light scattering theory [20]. The $D(4,3)$ index was chosen instead of $D(3,2)$ since it is very sensitive to the presence of small amounts of large particles.

2.4. Electrophoretic mobility measurement

The electrophoretic mobility (μE) was measured every 2 h during emulsification using Malvern Zetasizer Nano ZS (Malvern instrument, Worcestershire, UK). Measurements were performed on standard capillary electrophoresis cell equipped with gold electrodes. Electrophoretic mobility of emulsion droplets evaluated the surface charge of oil droplets. The mobility of emulsion droplets was measured by diluting emulsion (0.05%) ultrafiltrated water. The measurements were an average of 20 runs (equilibration time: 10s, number of run: 20, run) and quoted result is the average of 3 different measurements. Measurements were carried out at 25 °C. Measurements were performed directly in the diluted emulsions and results were averages of triplicate analyses.

2.5. Emulsions pH

Emulsion pH was measured every 2 h using a pH meter Lab 850 (Schott instrument, Deutschland, Germany) for all oil concentrations. Each measurement was performed on five different samples.

2.6. Turbidity measurement

Turbidity measurement was performed with a turbidimeter (Analyte NEP 160 VanMc Instruments turbidimeter, Mulgrave, Australia) equipped with a probe-type CIP160-3 and counter anal NEP260. The probe was immersed in emulsion to measure mixture turbidity; the measurement was made in triplicate.