



Role of emulsifier layer, antioxidants and radical initiators in the oxidation of olive oil-in-water emulsions

Monica Mosca*, Francesca Cuomo, Francesco Lopez, Andrea Ceglie

Dipartimento di Agricoltura, Ambiente ed Alimenti (DIAAA) and CSGI (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase), Università degli studi del Molise, I-86100 Campobasso, Italy

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ABSTRACT

Lipid oxidation in oil-in-water (O/W) emulsions is largely affected by the properties of the interfacial layer surrounding the oil droplets. In this work, the effect of the emulsifier layer structure, presence of both hydrophilic and lipophilic antioxidants and radical initiators on the development of lipid oxidation in olive oil-in-water emulsions was investigated. The olive oil-in-water emulsion is a suitable model of low fat food emulsions. The rationale of the work was to study the role of the interfacial layer when both the antioxidants and the radical initiators came from the two different emulsion compartments. Emulsions were prepared by using food grade emulsifiers of the Tween series (polyoxyethylene sorbitan esters) in the water phase and Span 80 (sorbitan monooleate) in the oil phase. The properties of the interfacial layer were changed by using Tween 20, Tween 60, Tween 80, which have different hydrophobic tails. These systems were oxidized by means of both hydrophilic (AAPH (2,2'-azobis(2-methyl-propanimidamide dihydrochloride)), AIPH (2,2'-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride) and lipophilic (AMVN (2,2'-azobis(2,4-dimethylvaleronitrile))) radical initiators at 40 °C. A continuous fluorescent method based on the front face technique allowed us to follow directly the development of oxidation in the whole emulsion. The combination Tween 80/Span 80 produced an interfacial layer more resistant to radical attack. Moreover, a polar paradox was verified also for radical initiators, while the results suggest that the best way to protect emulsions is to use a combination of antioxidants in both phases, to promote a synergy and the regeneration of antioxidants mediated by the interfacial layer.

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1. Introduction

In food products, natural and processed lipids are frequently used in the form of emulsions (McClements, 2005). Emulsions consist of two or more immiscible or partially miscible liquids (such as lipid and water) with one liquid being dispersed in the other in the form of droplets (Friberg & Kayali, 1991; McClements & Decker, 2000; Mosca, Murgia, Ceglie, Monduzzi, & Ambrosone, 2006; Venditti, Cuomo, Ceglie, Ambrosone, & Lopez, 2010). While emulsions are thermodynamically unstable systems, they can be kinetically stabilized using emulsifiers.

Emulsifiers are amphiphilic molecules that readily adsorb and accumulate at the interphase between the dispersed phase (e.g., lipid) and the continuous phase (e.g., water) of an emulsion (e.g., oil-in-water). Emulsifiers decrease the interfacial tension and produce repulsive interactions between droplets to prevent droplet aggregation or coalescence (Monduzzi, Ceglie, Lindman, & Soderman, 1990). They can also prevent

droplet aggregation by sterical hindrance due to large polar neutral groups exposed on droplet surface. The role of emulsifiers can be also important for the prolongation of the initial structure which determines also some food emulsion characteristic like flavor, odor, and nutritive value. In fact the rate of lipid oxidation in emulsion can be controlled by changing the characteristics of the interfacial layer which can act as a physical barrier separating pro-oxidants from the water phase and hydroperoxides in the oil phase (Kargar, Spyropoulos, & Norton, 2011). During the oxidation of lipids in heterogeneous systems the formation of oxidation products may be affected by emulsion structure because it determines the local concentration of both reagents and products of the oxidation reactions. Lipid hydroperoxides are surface-active compounds and are thus able to accumulate at the lipid–water interphase of emulsion droplets. The existence of pro-oxidants in the aqueous phase and lipid hydroperoxides at the emulsion droplet surface suggests that lipid oxidation in oil-in-water emulsions primarily occurs at the emulsion droplet interphase (Ambrosone, Mosca, & Ceglie, 2007). All these things considered, the thorough comprehension of the factors affecting lipid oxidation in heterogeneous systems such as emulsions, may lead to the attainment of tools for the protection of complex foods from deterioration. In food emulsions the achievement of an adequate structure together with oxidative and physical stability upon storage is a main issue. Vegetable oils are widely used in food emulsions

* Corresponding author at: Dipartimento Agricoltura, Ambiente ed Alimenti (DIAAA) and CSGI (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase), Università del Molise, via De Sanctis, I-86100 Campobasso, Italy. Tel.: +39 0874404635; fax: +39 0874404652.

E-mail address: mosca@unimol.it (M. Mosca).

because of their technological and sensory properties but they are more prone to oxidation due to unsaturated fatty acids. Among others, extra virgin olive oil use is preferable because of its lower unsaturation and its antioxidant content (Ambrosone, Cinelli, Mosca, & Ceglie, 2006; Xenakis, Papadimitriou, & Sotiropoulos, 2010). With this respect, it is important to study the effects of the main factors that can influence the occurrence of the oxidation reaction in a system when different phases, e.g. aqueous and oil phase, are present (Mosca, 2010; Mosca, Ceglie, & Ambrosone, 2008a, 2008b, 2011). As it has been said before, the emulsifier layer at the oil in water (o/w) interphase may play a crucial role in the oxidation reaction. Then, in oxidation studies it is convenient to use radical initiators that decompose thermally to give a constant flux of radicals with time. In this way the initiation step of the chain reaction is controlled and the corresponding rate can be easily calculated. Moreover the use of radical azo-initiators allows us to accelerate the oxidation reaction at lower temperatures ($\sim 40^\circ\text{C}$) with respect to other accelerated oxidation methods such as rancimat and oxygen bomb. In this way the physical characteristics of emulsions during the evolution of the oxidation reaction can be monitored because the oxidation conditions are not so drastic to promote emulsion degradation and separation (Mosca, 2010). The interfacial layer can also affect the effectiveness of antioxidants where they are located in one of the phases of emulsion (Mosca et al., 2008a). In fact the effectiveness of antioxidants in food emulsions depends on both their chemical and their physical properties. The importance of physical properties has been highlighted by the "antioxidant polar paradox" that states that non polar antioxidants are more effective in oil-in-water emulsions while polar antioxidants are more effective in bulk oils (Porter, 1993). In oil-in-water emulsions, non polar antioxidants are thought to be more effective because they are present in higher concentrations in the oil droplet (Huang, Hopia, Schwarz, Frankel, & German, 1996). On the other hand, polar antioxidants readily partition into the aqueous phase, decreasing their concentration in the lipid phase and thus lowering their capability to prevent oxidation. However, the effectiveness of antioxidants in oil-in-water emulsions could also be dependent on their surface activity and ability to accumulate at the oil-water interphase where oxidative reactions are most prevalent (Liu & Yang, 2008; Nuchi, McClements, & Decker, 2001). Recent papers on this topic, have demonstrated that ascorbic acid dispersed in the aqueous phase of w/o emulsions is effective in delaying the oxidation reaction and that its activity depends on its concentration and on the specific surface area of dispersed water phase (Mosca et al., 2008a). Therefore, the choice of the antioxidant to protect multiphase systems is often challenging because the activity of antioxidant is influenced by the composition of the phases and interphases. In particular, main importance has to be given to the physical properties of the dispersed phase, especially droplet size distribution, concentration and composition (Ambrosone, Mosca, & Ceglie, 2006; Ambrosone et al., 2007; Cuomo, Ceglie, & Lopez, 2012; Mosca et al., 2008a). All these factors may affect the partitioning behavior of antioxidant and also their effectiveness with storage time, since they will undergo oxidation as well as the oil phase. All these things considered, in this work, the oxidation stability of olive oil-in-water emulsions was studied as a function of the type of emulsifier of the Tween (polyoxyethylene esters) series, radical initiator and antioxidants added in both compartments. The use of olive oil of a standard composition according to the European Pharmacopoeia makes the o/w emulsions studied here a suitable model of low fat foods with emulsion structure. Recently, many works have investigated the role of interfacial microstructure in the oxidation of o/w emulsions in presence of biopolymers and particles (Charoen et al., 2012; Kargar et al., 2011). In this context, further study is needed to understand how the large emulsion interphase affects the oxidation reaction when antioxidants and prooxidants are dissolved in the two compartments of o/w emulsions.

The aim of this work is to find simple and effective ways to monitor and control lipid oxidation in multiphase food systems by varying

some key parameters of emulsion composition. To fulfill the scope, the interfacial layer was modulated by using Tween emulsifiers at different Hydrophilic Lipophilic Balance (HLB) while both hydrophilic and lipophilic azo-initiators were used to study the effect of prooxidants polarity on the overall kinetics of oxidation. In fact, the lipophilic 2,2'-azobis(2,4-dimethylvaleronitrile), AMVN, was used to trigger the oxidation reaction in the oil phase while the hydrophilic 2,2'-azobis-2methyl-propanimidamide dihydrochloride, AAPH and 2,2'-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride, AIPH were used to produce radicals in the aqueous phase. To test the effectiveness of antioxidants in a radical initiated oxidation reaction of oil-in-water emulsions, ascorbic acid was used as the hydrophilic antioxidant, while ascorbyl palmitate and vitamin E were added in the oil phase. Moreover, we used a new continuous fluorescent method to follow the oxidation in o/w emulsions without the need of withdrawing the sample for further treatment and hydroperoxides measurements (Tikekar, Johnson, & Nitin, 2011; Tikekar & Nitin, 2011, 2012). In this way, the emulsions can be analyzed *in toto* so having a real time sketch of the oxidation process. The oxidation results were related to the size and z-potential measurements in order to study the changes in emulsion structure due to the oxidation process.

2. Materials and methods

2.1. Materials

Polysorbate 80 (Polyoxyethylene 20 sorbitan monooleate, Tween 80), Tween 20 (polyoxyethylene 20 monolaurate), Tween 60 (polyoxyethylene 20 monostearate), Sorbitan monooleate (Span 80) were from Fluka analytical. The olive oil (*Olivae oleum Virginale*) of composition and purity according to the European Pharmacopoeia, vitamin E and ascorbyl palmitate were from Fluka. Ascorbic acid was from Sigma Aldrich. The radical initiator 2,2'-azobis(2,4-dimethylvaleronitrile), AMVN, was from Cayman Chemical Company. AAPH (2,2'-azobis-2methyl-propanimidamide dihydrochloride amide dihydrochloride), AIPH (2,2'-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride) were from Wako Chemicals GmbH. The fluorescence probe diphenyl-1-pyrenylphosphine (DPPP) was from Probiol. All reagents used were of analytical grade.

2.2. Methods

2.2.1. Emulsion preparation and oxidation

Olive oil-in-water emulsions were prepared with deionized water at pH 7.4 (phosphate buffer). In particular, emulsions contained 1 wt% of olive oil with 1 wt% Span 80. The aqueous phase contained 1 wt% of Tween surfactants with different hydrophobic tails (Tween 20, Tween 60, Tween 80, respectively). The fluorescent probe was added to the oil phase prior to emulsification as chloroform-methanolic solution in order to have a final concentration of DPPP of 80 $\mu\text{mol/g}$ (300 μl of DPPP 2.7 mM in 3 g emulsion). The resulting solution was evaporated under N_2 to eliminate the solvent completely. The hydrosoluble radical initiator AAPH or AIPH (0.4 wt%) was added directly to the water phase, while the liposoluble AMVN was added to the oil phase, before the emulsification process. The emulsions were prepared by mixing with Ultraturax T8 for two minutes at 24×10^3 rpm. The kinetics of oxidation was followed in continuous at the fluorimeter at 40°C . Since the emulsions were turbid, the front face geometry was used for the fluorescence measurements at 380 nm ($\lambda_{\text{ex}} = 352$ nm).

2.2.2. Monitoring the oxidation: fluorescence spectroscopy

Oil oxidation was monitored with time by using a fluorimetric method which exploits the fluorescent probe indicated in Akasaka et al. (Akasaka, Sasaki, Ohru, & Meguro, 1992; Akasaka, Takamura, Ohru, Meguro, & Hashimoto, 1996). DPPP is reported to be a fluorescent reagent for the measurements of hydroperoxides with high

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