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THE EFFECTS OF SURFACTANTS ON THE OXIDATION OF SUNFLOWER OIL IN EMULSIONS

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Abstract

Lipid oxidation in O/W emulsions take places mostly at the interface of oil and water, therefore the types and properties of emulsifiers accumulating at the droplet interface have a large effect on the oxidative stability of oils in emulsions. In this study, 5% sunflower oil in water emulsions were produced by ultrasonic homogenizer (300 W, 5 min) with different emulsifiers (sunflower lecithin, whey protein isolate, whey protein concentrate, citrus pectin, Tween 80 (T80), and the mixture of T80 and Span 20 (S20) at two different pH (4 and 7). The particle size, zeta potential and oxidative stability of emulsions (Induction Period, IP) were measured. IP values were determined by the OXITEST® reactor which subjects the sample to an oxidative stress environment at high temperature (90°C) and high oxygen pressure (6 atm), and the higher IP value showed higher resistance of the sample to the oxidation. The smaller particle sizes (108.5 – 282.3 nm) were obtained by using small molecule surfactants. Zeta potential of lipid droplets had more negative values at pH 4. IP value was the highest at lecithin stabilized emulsions at both pH values, followed by protein stabilized emulsions at low pH. The mixture of S20 and T80 provided more oxidative stabilization compare to the using T80 alone at both pH values. Pectin stabilized emulsions were least stable to the oxidation among samples. The study showed that particle size had no apparent effect on the oxidation, whereas the type of emulsifier and pH had a significant effect on lipid oxidation.

Keywords: oxitest, oxidation, o/w emulsion, emulsifier

1. Introduction

Food formulations often contain a lipid phase dispersed in an aqueous medium, that can be classified as oil-in-water (O/W) emulsions. From their manufacture to their end-use, food emulsions are subjected to a broad range of physical-chemical treatments. Therefore, the susceptibility of lipid to oxidation is a major concern for food manufacturers as lipid oxidation has negative effects on food quality such as; taste, appearance, texture and shelf life. Lipid oxidation leads to the development of off-flavours (rancidity) and toxic compounds. Food emulsions are stabilized by surface-active molecules that adsorbed at the oil-water interface. Surfactants have required the ability to facilitate the formation and stabilization of fine oil droplets during and after emulsification due to their surface activity at the oil-water interface.
The oxidative stability of emulsions is measured by various methods (Karadag et al., 2017), including the spectrophotometric determination of peroxide value, conjugated diene and trienes; GC analyses of volatiles compounds (secondary oxidation products), free fatty acid or mono and diglycerides; HPLC evaluation of oxidized fatty acids. However, those methods including sample preparation steps require sophisticated analytical instruments and experienced analysts, and lipid oxidation is usually slow at room temperature and could take months to reach the rancidity threshold values. An interesting way to reduce the time of analysis of lipid oxidation compounds is using accelerated oxidation tests.

The OXITEST® reactor subjects the sample to an oxidative stress environment at high temperature and high oxygen pressure; the drop in oxygen pressure inside the oxidation chambers is monitored according to ability

of the food to oxidise and is expressed as the induction period (IP) which is theoretically defined as the time required to obtain a continuous oxidation cycle in the oxidation process; it is measured as the time required for a sudden and rapid change in the oxidation rate. It could be used alternatively to traditional and time-consuming methods with several advantages: analytical rapidity, easiness of use, reproducibility and reduced production of chemical wastes (Tinello et al., 2018).

The aim of this study, to characterize sunflower oil in water emulsions prepared by different surfactants sunflower lecithin, whey protein isolate, whey protein concentrate, citrus pectin, Tween 80, and the mixture of Tween 80 and Span 20 in terms of particle size, zeta potential at two different pH values (4 and 7), and determine their oxidative stability by an accelerated oxidation test.

2. Material and Methods

Sunflower lecithin was donated by Lipoid AG (Ludwigshafen, Germany); whey protein isolate and whey protein concentrate were provided from Arla Foods (Denmark); citrus pectin was provided from DSM (Turkey), Tween 80 and Span 20 was bought from Sigma Aldrich. 10 mM citrate (pH=4) and phosphate buffer (pH=7) was used as a continuous phase for emulsion and to dissolve surfactants.

2.1. Emulsion preparation

Surfactants were dissolved in buffer (pH 4 and 7) solutions and 5% sunflower oil was added. The mixture was homogenized by Ultra-Turrax dispersed (IKA, Germany) for 5 min., and fine emulsions were produced by the ultrasonic homogenizer (Hielscher, Germany) for 300 W at 5min.

2.2. Particle size and zeta potential measurement

Emulsions were diluted 100 times by the related buffers and particle size distribution and zeta potential values were measured by Zetasizer Nano ZSP (Malvern). The measurements were done at 25°C, three measurements were carried out on each sample.

2.3. Oxidative stability measurement

Oxidation of emulsion samples was monitored by “Oxitest” (Velp Scientifica, Usmate, Milan, Italy), equipped with two separated oxidation chambers. The sample was placed in a chamber; then this system was hermetically sealed, heated to 90 °C and pressurized oxygen (99.9999% purity) was injected into Chamber. The analysis was initiated after the oxygen pressure reached to 6 atm. The Oxitest reactor monitors the absolute pressure change inside the chambers calculating the oxygen uptake of the oxidizable compounds of the samples and automatically generates the Induction Period (IP). The higher the IP value shows, the higher the resistance of the sample is to oxidation.

3. Results and Discussion

The particle size of sunflower oil in water emulsions prepared by different surfactants was given in Table 1. The high interfacial area due to smaller particle sizes makes oil droplets more susceptible to oxidation. Emulsions stabilized by low molecular weight surfactant had smaller particle size between 100 and 280 nm at 2 pH values studied. The lowest particle size obtained with the mixture of hydrophilic and hydrophobic emulsifiers with different HLB values, Tween 80 and Span 20 respectively. When different types of emulsifiers were compared hydrocolloid emulsifiers (WPI, WPC and pectin) clearly resulted in larger droplets compared to low molecular weight emulsifiers (Tween 80 and Lecithin). This is possibly related to their larger molecular size and low adsorption ability to the oil-water interface (Gomes et al., 2018). WPI stabilized emulsions, however at neutral pH had also particle size lower than 250 nm, whereas the size was around 5µm at acidic pH. This was associated with the increased solubility of proteins at neutral pH values.

Therefore, oil droplets stabilized by both WPI and WPC at pH 7 had smaller particle sizes compared to those prepared at pH 4.

Table 1. Particle size of sunflower oil in water emulsions prepared by different surfactants

	Particle size (μm)	
Emulsion samples	pH=4	pH=7
Tween 80	0.146±0.00	0.154±0.00
Tween 80 + Span 20 (1:1; w:w)	0.265±0.00	0.109±0.00
Lecithin	0.282±0.00	0.186±0.00
Pectin	1.793±0.13	1.898±0.39
Whey Protein Isolate (WPI)	4.994±0.72	0.241±0.00
Whey Protein Concentrate (WPC)	5.750±1.31	0.710±0.04

Zeta potential values of sunflower oil in water emulsions prepared by different surfactants were given in Figure 1. Zeta potential is the potential difference between the mobile dispersion medium and the stationary layer of the dispersion medium attached to the dispersed particle. Emulsions with high zeta potential (negative or positive) are electrically stabilized while emulsions with low zeta potentials (30 mV) tend to coagulate or flocculate.

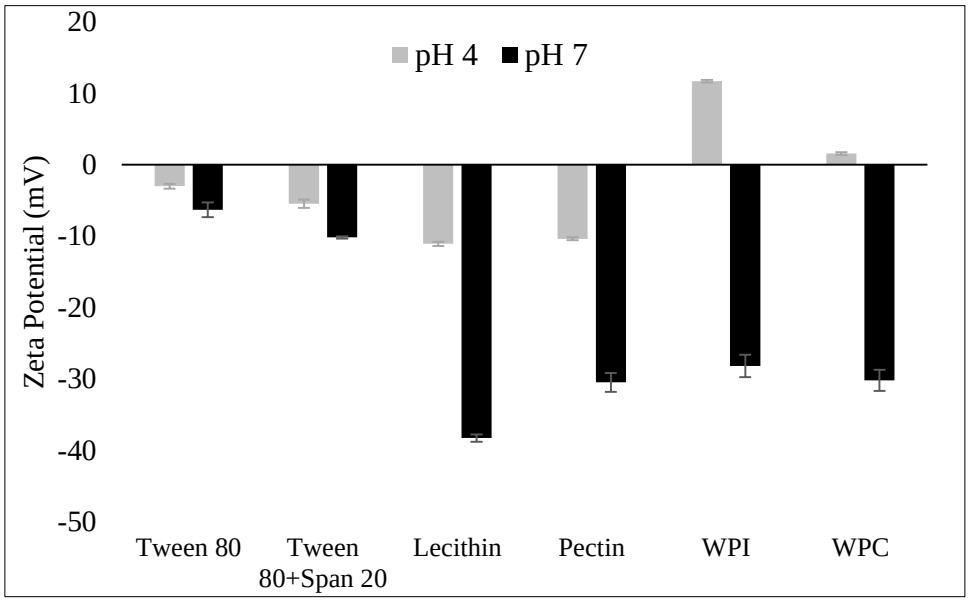

Figure 1. Zeta potential values of sunflower oil in water emulsions prepared by different surfactants

Proteins had negative charges at pH values higher than their isoelectric points. Therefore, at neutral pH values, higher negative zeta potential values were observed. Zeta potential values around zero show that the isoelectric point of WPC is close to pH 4. Pectin is an anionic polysaccharide, neutral pH favoured higher zeta potential values for the surfaces of oil droplets.

Induction points (IP) of emulsions prepared by different surfactants were given in Table 2. Oxidative stability of the emulsions is one of the crucial factors determining the shelf life of the products. Several factors such as oil types, formulation and pH, oxygen concentration, antioxidants, interfacial characteristics, and droplet characteristics affect the oxidative stability of emulsions. IP value of our samples ranged from 67 to 805 min, meaning higher IP values showed higher stability to oxidation. Phospholipids have metal-

chelating properties and ability of quenching of singlet oxygen and can limit the permeation of free radicals across the emulsion interface. It may be the reason for being the most oxidative stable formulations prepared by lecithin at two pH values.

In terms of stability at different pH, it was higher when the pH was 4 in hydrocolloid stabilized emulsions. Higher pH values could result in low iron solubility and precipitation of the metal ions on the lipid droplet surface, and closer contact with lipid phase occurred (Berton-Carabin et al., 2014). In addition to that, as seen in Figure 1 at pH 7, droplets had higher negative zeta potential values, hence they can attract positively charged transition metal ions and promote lipid oxidation compared to emulsions with lower pH values. Natural antioxidants, e.g. α-tocopherol, found in sunflower oil was more effective at low pH due to its increased hydrogen donation capacity.

Table 2. Induction points of sunflower oil in water emulsions prepared by different surfactants

	Induction point (min)	
	pH=4	pH=7
Tween 80	401±22	431±16
Tween 80 + Span 20	551±14	503±22
Lecithin	805±32	731±27
Pectin	383±26	67±9
WPI	686±40	365±32
WPC	586±33	488±42

Pectin promoted the lipid oxidation in emulsions at high pH, having the lowest IP (Table 2). Negative charges of free carboxyl groups in pectin molecules can form covalent bonds with the valence divalent metal ions (Qui et al., 2012). Therefore, low pH would favour protonation of the carboxyl sites (less negative values), leading to reduced metal-binding activity and less oxidation at pH 4 was observed compared to samples at pH 7.

Proteins can act as metal chelators or metal binders in dispersed systems that depend on their charge and solution pH. Proteins are anionic at pH's above their isoelectric point, hence they can able to bind positively charged ferrous ions. Amino acid residues of proteins can also trap free radicals produced in the aqueous phase (Dickinson, 2009). Therefore at pH 4 protein stabilized emulsions showed better oxidative stability after lecithin.

4. Conclusion

The results of this study showed that the types of emulsifiers and pH are important in terms of determination of the emulsions susceptibility to lipid oxidation. Lecithin, due to phospholipids in its composition, stabilized emulsions showed the highest stability and whereas the use of pectin promoted oxidation in emulsions. The oxidative stability of oil in water emulsions can be measured by an accelerated oxidation test, though in the following study this should be confirmed with traditional analytical methods applied for the measurement of the primary and secondary oxidation products.

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