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Review

Review on the Antioxidant Activity of Phenolics in o/w Emulsions along with the Impact of a Few Important Factors on Their Interfacial Behaviour

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Abstract: This review paper focuses on the antioxidant properties of phenolic compounds in oil in water (o/w) emulsion systems. The authors first provide an overview of the most recent studies on the activity of common, naturally occurring phenolic compounds against the oxidative deterioration of o/w emulsions. A screening of the latest literature was subsequently performed with the aim to elucidate how specific parameters (polarity, pH, emulsifiers, and synergistic action) affect the phenolic interfacial distribution, which in turn determines their antioxidant potential in food emulsion systems. An understanding of the interfacial activity of phenolic antioxidants could be of interest to food scientists working on the development of novel food products enriched with functional ingredients. It would also provide further insight to health scientists exploring the potentially beneficial properties of phenolic antioxidants against the oxidative damage of amphiphilic biological membranes (which link to serious pathologic conditions).

Keywords: antioxidants; phenolics; emulsions; interfacial distribution

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1. Introduction

Lipid oxidation is a serious problem for scientists since it adversely affects the product quality in the food, cosmetic, and pharmaceutical sectors [1]. Many common food products exist as oil-in-water (o/w) emulsions including beverages, dressings, sauces, soups, and desserts [2]. One of the main causes of the quality deterioration of these products is the oxidation of lipids [3]. The degradation of unsaturated lipids can lead to off-flavors, decreases the nutritional profile of foods, and may eventually generate toxic products [4]. In emulsified foods, lipid oxidation can occur rapidly due to their large surface area, with mechanisms that are more complex and not fully understood compared to bulk oils [5,6]. As a consequence, the food industry faces a serious problem due to the low oxidative stability of emulsified systems, which adversely impacts consumer safety and the economic viability of the products [7]. A better understanding of the endogenous and exogenous factors that monitor the microstructural and oxidative stability of food emulsions would help to maintain their desirable functional and sensory properties during the formulation, processing, and storage of relevant products [8]. In addition, emulsion systems generally mimic the amphiphilic nature of important biological membranes (such as lipoproteins) that are prone to oxidative degradation when attacked by singlet oxygen and free radicals [9]. This biochemical process eventually links to the development of serious human health conditions, such as aging, carcinogenesis, and cardiovascular diseases [10].

Over the last few years, there is a steady food market trend for the use of natural antioxidants, as a common strategy to slow down lipid oxidation in emulsified foods, increase their shelf life, and minimize bad odors [11,12]. A body of recent research [13,14] focuses on nano-emulsions that are increasingly used in various products in order to incorporate easily degradable bioactive compounds, protect them against oxidation, and enhance their bioavailability. In manufactured products (quite often heterogeneous systems containing lipids as emulsions or bulk phase) the efficiency of an antioxidant is determined not only by its chemical reactivity, but also by its physical properties and its interaction with other compounds present in the products [15].

With the term phenolics, we refer to a wide class of natural compounds (e.g., tocopherols, flavonoids, phenolic acids) with varying structures and antioxidant properties [16]. The application of phenolic compounds in various commercial products has attracted an increasing level of interest over the last few years from researchers in the food, pharmaceutical, and nutraceutical industries [17]. It is true, though, that certain structural characteristics (including the hydrophobic character of many phenolics) may affect their integration into real products as well as their general biological activities and their bio-absorption in human organisms [18]. Their potential to act as functional ingredients upon their addition in bulk or emulsified oils has been an area of emerging scientific interest in the last decade [19–21]. A few researchers in this field have focused on phenolic acids, their activity, health effects, and extraction from natural plant sources [21–23]. Phenolic acids are classified as hydroxybenzoic and hydroxycinnamic acids, and, depending on their structure, may present solubility in water or lipids, thus enabling their use in many products [7,14,24].

In this review paper, the authors focus on the antioxidant properties of phenolic antioxidants against the oxidative deterioration of food-relevant o/w model emulsions. The novelty of this paper mainly concerns the literature review of the most important interfacial factors that determine the antioxidant potential of phenolic compounds in food emulsion systems. The phenolic distribution is determined by solubility and partitioning behaviour in the different regions of the emulsion (oil core, aqueous phase, interface) and together with the mode of incorporation can significantly determine the antioxidant efficiency [25,26]. The interfacial synergistic activity of various phenolic antioxidants is also discussed as an additional important factor. Further to the technological importance of phenolics and the protection against oxidative deterioration as a result of their incorporation in real lipid-based products, there is also an additional aspect. The research findings from phenolic activity in interfacial systems could be of interest to clinical nutrition researchers who explore the potential effects of natural antioxidants against the oxidative damage of amphiphilic biological membranes.

In addition, the analysis of such research outcomes can feed the development of novel food emulsions and thereby trigger innovation and new market applications in the associated industrial sectors.

2. Overview of Studies Reporting on the Effect of Phenolics against the Oxidation of o/w Emulsions

Although most of the studies on phenolic antioxidants so far have focused on bulk oils, a body of recent research has examined the activity of various phenolic compounds in food-related o/w emulsions. In emulsified systems, the initial step of lipid oxidation takes place at the interface between the oil and water phases. Over the last few years, an increasing number of researchers have reported well-documented antioxidant activities of naturally occurring phenolics in o/w model systems [19,27].

Tocopherols are a class of natural compounds with a high nutritional value in the human diet because of their vitamin E activity. In addition, various authors have reported their well-established antioxidants activity in vitro (oil model systems) and in vivo (human clinical trials) [28,29]. Wang et al. [30], following oxidation experiments of flaxseed o/w emulsions, have noted a higher antioxidant efficiency of δ-tocopherol compared to α-tocopherol. The authors linked the superior activity of δ-tocopherol to its enhanced distribution in the interfacial area of the emulsion system. Another similar study—based on the autoxidation of shrimp o/w emulsions under storage at room temperature did not report any protective effect of α-tocopherol against oxidative destabilisation [31]. On the contrary, α-tocopherol when combined with chitooligosaccharides (at both 0.2 and

0.4 g/L concentrations) significantly delayed the oxidation process, in terms of both primary (conjugated dienes) and secondary (TBARs) oxidation products indicators [31]. Barouh et al. [15] further explored the activity of tocopherols in bulk oils and emulsion systems as a function of various physicochemical parameters (including their interaction with specific emulsifiers such as Tween 65, Tween 80, whey proteins, etc.).

Flavonoids comprise another class of widespread phenolic compounds with well-established antioxidant properties strongly related to their structure [32,33]. Common plant flavonoids such as quercetin, rutin, and hesperitin prolong the shelf life of o/w emulsions by retarding the oxidative deterioration and improving physical stability. However, only quercetin retained its antioxidant activity in the presence of ferric ions due to its structural configuration (3′4′ dihyrdoxy substitution of B ring and the presence o 3-OH) [34]. In fact, quercetin seems to be one of the most potent contributors to the antioxidant activity of plant extracts in emulsions [35]. However, quercetin has been reported to exert a pro-oxidant character in pure lipids and antioxidant activity in emulsions due to its hydroxyl group in position-3 [36]. Catechin acted as a better antioxidant than quercetin in the copper-induced oxidation of diluted, Tween-based, linoleic acid emulsion (0.02 M), while morin presented the best protective action [37]. Different metal ions may affect the activity of flavonoids in emulsions, where the pro-oxidant or antioxidant character may dependon the flavonoid structure and the metal type [38] Flavonoids have also been examined for the preparation of physically stable pickering emulsions, while also offering oxidative stability [39,40].

Plant extracts are rich in flavonoids and phenolic acids and exert a strong antioxidant activity in o/w emulsions that may be attributed to synergism among its components and also to partitioning in the aqueous phase (e.g., polar phenolic acids or flavonoid glycosides), oil-water interface (e.g., medium polarity phenolic acids and flavonoids), or the oil phase (e.g., flavonoid aglycons) of the emulsion [41,42]. Additionally, the presence of endogenous antioxidants such as α-tocopherol may affect the flavonoid activity in lipid systems; e.g., it showed a strong synergistic effect with quercetin in emulsions, and a clear antagonistic effect in bulk oil [43]. More information on the phenolic synergistic effects is given in Section 3.4.

The current paper has focused on various phenolic acids available in many natural sources (e.g., in olive oil, herbs, fruits) that have been widely explored in food systems [44]. Caffeic acid (CA) is perhaps the most well-known phenolic acid widely spread in the plant kingdom [45]. CA exerted a clear antioxidant effect when added in o/w emulsion systems stabilised by Tween and prepared with various vegetable oils [46,47]. Ferulic acid (FA) is another phenolic acid -commonly present in many plant seeds [48] that was reported to act as a strong antioxidant following its addition in a range of oil-based emulsions [49–51].

For gallic acid (GA), which is found in high amounts in tea and berries [52] there is some contradictory evidence in the literature about its protective action against oxidation of food emulsions. GA and its alkyl esters were found to exert a clear antioxidant effect against the oxidation of rapeseed o/w nano-emulsions stabilised by SDS [53] or even double emulsions by the use of encapsulation [54]. Additionally, Zhu et al. [55] concluded a strong inhibitory effect of GA and its alkyl esters against the formation of both primary (Peroxide Values) and secondary oxidation products (hexanal content). Propyl gallate exerted a superior activity compared to gallic acid and the other gallate esters. Other studies, however, did not report any protective effect of GA in o/w emulsions [56,57].

A large variety of plants and vegetables are abundant in p-coumaric acid (p-CA) [58]. Park et al. [59] reported that roasted rice hull extracts, with a high concentration of p-CA enhanced the oxidative stability of bulk oil and o/w emulsions at 60 °C. Rosmarinic acid (RA) is the main phenolic component in various edible and aromatic herbs of the Lamiaceae family (including *Rosmarinus officinalis*, *Origanum* spp., etc.) [60]. Choulitoudi et al. [19] observed that ethanol and ethyl acetate extracts of *Satureja thymbra*—articularly rich in RA—reduced by 75–80% the oxidation rate of sunflower o/w emulsions at chilling temperature (5 °C). Other researchers reported the antioxidant activity of RA in corn oil-and soyabean oil-based emulsions [61,62] as well as in a model emulsion system based on linoleic acid [46].

Bakota et al. [63] incorporated either pure RA or RA-rich extract (from *Salvia officinalis* leaves), at a concentration of ~30 mg/g, into o/w emulsions and observed that both treatments were effective in suppressing lipid oxidation.

Vanillic acid (VA) is a phenolic acid found in several fruits, olives, and cereal grains. Keller et al. [64] observed a strong antioxidant character of VA during the autoxidation of Tween 40-based o/w systems, at pH 3.5. In addition, a few authors [30,65] reported that the addition of tannic acid (TA) enhanced the resistance of plant-based emulsions against both droplet aggregation and lipid oxidation as a result of its strong ferrous ion-binding properties.

Ascorbic acid is another phenolic compound widely present in nature and with a high nutritional value (also known as vitamin C). A number of scientists highlighted the important role of ascorbic acid in antioxidant synergies examined in both food and clinically relevant studies [66,67].

As will be discussed under Section 3.4, a shift from the prooxidant to an antioxidant potential of ascorbic acid in interfacial systems is vastly dependent on the presence of other phenolic compounds in the system (and in particular of tocopherols).

3. Interfacial Factors That Affect the Antioxidant Activity of Phenolic Compounds

Various authors examined a number of factors that can potentially influence the physical and oxidative stability of emulsions including type and concentration of oil phase and of emulsifiers, pH and ionic composition, emulsion droplet size, and interfacial properties [68,69]. Raikos et al. [70] noted that the physical location of antioxidants in o/w emulsions can have a significant influence on their free radical scavenging activity and ability to inhibit lipid oxidation. The partitioning of antioxidant molecules in emulsions has been reported to affect their activity [71]. According to Shahidi and Zhong [6], the efficacy of antioxidants in emulsified systems is determined by their polarity but also by their molecular size, mechanism of action, and the presence and type of emulsifiers. Kiokias and Oreopoulou [72] explored the antioxidant effect of carotenoids with varying polarities in sunflower oil-in-water emulsions. The authors attributed the superior antioxidant effect of polar carotenoids to their enhanced distribution in the interface of the emulsion system and claimed that less potent β-carotene is likely to be homogeneously dispersed in the oil droplets. On the contrary, the polar xanthophylls (lutein, and annatto carotenoids) may be located near the oil-water interface where their hydrophilic groups (-OH, COOH, etc.) are better orientated, and thereby more efficiently trap the AAPH-derived radicals attacking from the water phase of the emulsion.

The authors note that a similar mode of action is also expected to occur during the action of phenolic antioxidants in an emulsion system. Figure 1 provides a general picture of the expected distribution of an amphiphilic phenolic antioxidant in the emulsion phases. The alkyl chain (hydrophobic part) is mainly oriented towards the lipid core of the oil droplet, whereas the hydrophilic part (with OH/COOH groups) is preferentially located towards the interfacial region of the emulsion phase. The most important interfacial factors that determine the antioxidant potential of phenolic compounds in food emulsion systems are examined in the following sections.

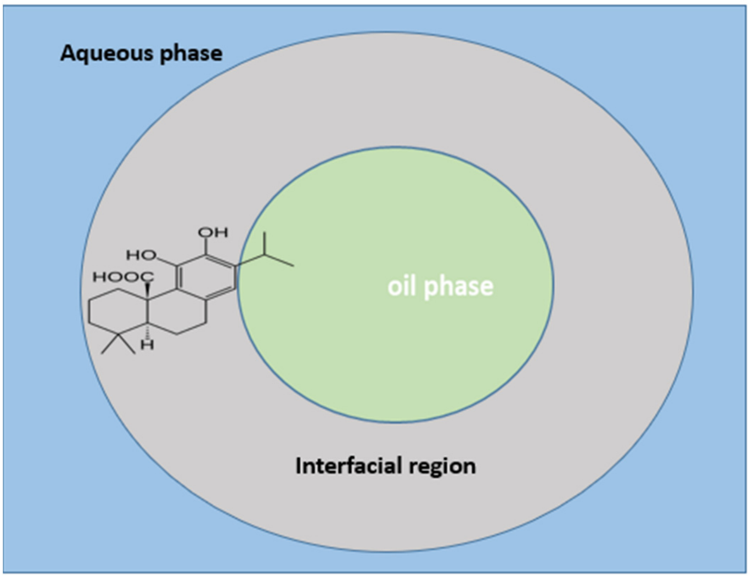


Figure 1. Expected partitioning of phenolic antioxidants between the different regions of an o/w emulsion system (alkyl chain towards the lipid core, hydrophilic part towards the interface).

3.1. Effect of pH of the Aqueous Phase on the Interfacial Activity of Phenolic Compounds

There is a general agreement about the important role of pH in monitoring the microstructural stability of food-relevant emulsion products [73]. However, how pH affects the oxidative destabilisation of emulsions is pending some further clarification due to contradictory evidence in the relevant literature [4].

Interestingly, Branco et al. [74] observed that a pH change from 3.0 to 7.0 increased the peroxide value (PV) and reduced the thiobaribituric acid reactive substance (TBARS) in o/w emulsions. The authors noted, though, that the presence of ascorbic acid (1 mmol/L) not only had no significant inhibitory effect on PV and TBARS ($p < 0.05$), but even triggered a prooxidant character. Costa et al. [75] noted that a modification of the pH in the aqueous phase could largely affect the interfacial distribution, and consequently the antioxidant activity, of phenolic acids.

Zhou and Elias [76] reported that the pH is capable of influencing the antioxidant activity of phenolics, along with transition metal properties, and is overall a factor to take into careful consideration in the production of food-relevant emulsion systems. The results of Sorensen et al. [77] indicated that the pH, especially in the presence of iron, had a greater impact on lipid oxidation than the size of the lipid droplets. CA promoted oxidation at pH 3 in the presence of iron, a fact attributed to its ability to reduce Fe^{3+} to Fe^{2+}, thereby propagating lipid oxidation and catalysing peroxide decomposition to the formation of secondary products. At pH 6, CA interacted and formed complexes with iron, as also observed for other phenolics, thus depressing PV formation, either with or without iron ions in the emulsion.

A similar study [78] concluded that in the presence of 25 μM Fe^{3+}, epigallocatechin gallate (EGCG), at a concentration of 400 μM, accelerated the oxidation of a Tween 80-stabilised flaxseed o/w emulsion at pH 3, but exhibited an antioxidant character at pH 7. Other researchers [79] observed that EGCG and epicatechin gallate (ECG)—even at lower concentrations (100 μM)—protected Tween-20 stabilised sunflower o/w emulsions from their oxidative degradation at pH 5.5, in the absence of Fe^{3+}. According to Kim and Choe [80], the oxidative degradation of soybean o/w emulsions proceeded faster at pH 4 in the absence of iron. Interestingly, the emulsions were more stable at the same pH compared to higher or lower acidity values when iron was present in the system. Upon addition of peppermint extract at pH 4, iron reduced and significantly delayed the degradation of total polyphenols (including RA and CA).

Tian et al. [81] reported that tea polyphenols, when added at a relatively low level, are located at the oil droplet surfaces in the whey protein-stabilised emulsions, because of their tendency to bind to the adsorbed protein molecules. Moreover, pH affects the potent synergistic actions of the phenolic acids with endogenous antioxidants as tocopherols. Kittipongpittaya et al. [82] observed that RA more effectively regenerated a-tocopherol at pH 7, due to its higher electron donation ability to the a-tocopheroxyl radicals at the oil-water interface, compared to pH 3. Losada-Barreiro et al. [83] investigated deeper the effects of pH on the partition constants and the distribution of GA and CA between the aqueous and interfacial regions of 10% corn oil/acidic water emulsions stabilised by Tween 20. The authors reported that a decrease in pH from 4 to 3 leads to an increase of GA distribution in the interface (from 20% to 60%), and of CA (from 50% to 75%) and concluded that acidity can exert a great impact on the partition of antioxidants between the emulsion phases. Similarly, a decrease in pH from 3.6 to 3 caused an increase in CA fraction in the interface from 90 to 95% [84]. These results may be attributed to the higher solubility of the phenolic ions (present at higher pH values) in the aqueous phase. A recent study [45] examined the antioxidant activity of GA and its alkyl esters in SDS-stabilised rapeseed o/w emulsions. GA, at pH 7, exerted a lower antioxidant effect than its ester derivatives. This was explained by the fact that GA at this pH is negatively charged and thereby repelled by the anionic SDS-coated interface, contrary to the electrostatically neutral ester derivatives. Furthermore, Zoric et al. [85] reported a lower stability of RA at pH 7.5 than at pH 2.5.

Overall, the pH of the aqueous phase plays an important role in determining the antioxidant effect of phenolic acids against the oxidative deterioration of o/w emulsion systems. In the absence of metals, a lower pH links to higher phenolic distribution in the interface leading to stronger antioxidant efficiencies. The situation, though, is more complex in the presence of transition metals in the emulsion system that seems to highly affect the role of pH on phenolic antioxidant activity. For instance, higher pH values overall induce metal-catalyzed oxidation by increasing the number of dissociated species. Another factor that can be crucial here is the formation of metal complexes with phenolic antioxidants and the change in oxidation potentials. Therefore, further investigation is needed to more precisely elucidate the mechanisms and actual effect of pH on the phenolic antioxidant activity in the presence of metals.

3.2. Effect of the Emulsifier and of the Interfacial Concentration of Phenolics on Their Antioxidant Activity

A few researchers have examined how certain features of the emulsifier may affect the lipid oxidation in food emulsions [86,87]. More specifically, the size and conformation of the emulsifier define the thickness of the emulsion droplet interface through the formation of biopolymer layers. In principle, the thicker the interfacial emulsifier layer, the more difficult for the free radicals to penetrate, thereby the better the antioxidant protection. This theory also explains why according to certain studies, low molecular weight emulsifiers (e.g., Tween, SDS) result in emulsions that are easier and faster oxidized compared to systems prepared under exactly the same experimental conditions but with larger molecular weight emulsifiers such as Brij 700 or certain proteins [88,89].

Among the possible environmental factors influencing the efficiency of phenolic antioxidants, the nature and concentration of surfactants was noted as the most important by McClements and Decker [90]. A few studies examined how emulsifiers may affect the partitioning of antioxidants in emulsions and thereby moderate their interfacial activities. Kiralan et al. [91] have suggested that surfactant micelles could increase the antioxidant activity of phenolics by changing their physical location. Other researchers in this field concluded that the location and concentration of phenolic antioxidants in the interface of an o/w model system are highly dependent on their molecular interaction with the present emulsifiers [26,62].

Da Silveira et al. [53] investigated the effect of the presence of surfactant micelles on the antioxidant efficiency of a homologous series of gallate phenolipids (with 0–16 carbon atoms alkyl chains: G0, G3, G8, G12, or G16) in o/w nano-emulsions. According to the results, the surfactant micelles hinder the antioxidant action of hydrophobic phenolipids, but not that of hydrophilic ones. Losada-Barreiro et al. [83] reported that a tenfold increase of the surfactant (Tween 20) volume enhanced the interfacial distribution of both GA (from 20% to 60%) and CA (from to 50% and 90%), thereby concluding that the emulsifier concentration largely determines the partition of phenolic acids in emulsified systems.

Keller et al. [64] examined the partitioning behaviour of VA following its addition in 30% o/w model systems stabilised by Tween 40 under low pH conditions (pH of aqueous phase: 3.5). The authors reported that when oil, water, and emulsifier were just mixed, the major proportion of VA (~90) retained in the aqueous phase was mostly associated with Tween micelles. In the homogenised emulsified system, though, VA migrated to the o/w interface of the oil droplet. Another study [49] focused on FA and iFA (isoferulic acid) trying to determine the parameters that affect their partitioning behaviour in the emulsion phases. According to the research findings, an increase in the concentration of the emulsifiers resulted in enhanced solubilisation and migration of both FA and iFA at the interface, which subsequently resulted in clear antioxidant activities of both tested phenolic acids. Furthermore, Mitrus et al. [14] concluded that a higher surfactant volume fraction increased the percentage of antioxidants distributed in the interface. Other researchers attempted to elucidate the protective action of a few proteins commonly used in food applications (e.g., whey proteins, soy proteins, etc.) against the oxidative destabilisation of emulsion systems. Such an antioxidant effect is highly dependent not only on the type, structure, and concentration of the protein but also on their synergistic action with other antioxidants (e.g., enhanced antioxidant activity of proteins mixtures with tocopherols and other phenolics) [4,92]. An overall conclusion of the relevant studies is that proteins may, indeed, affect the interfacial partitioning of phenolic antioxidants by modifying the interfacial charge [93]. In doing so, the proteins can alter the location of transition metal ions and their subsequent interaction with polyphenols thereby determining their antioxidant activity in the interfacial systems [94]. A picture of the microstructure for a protein stabilised emulsion (produced in NTUA/Laboratory of Food Chemistry and Technology) is given in Figure 2 (Confocal Laser Scanning Microscopy-CSLM image of a 10% cottonseed o/w emulsion stabilized by 1% sodium caseinate).

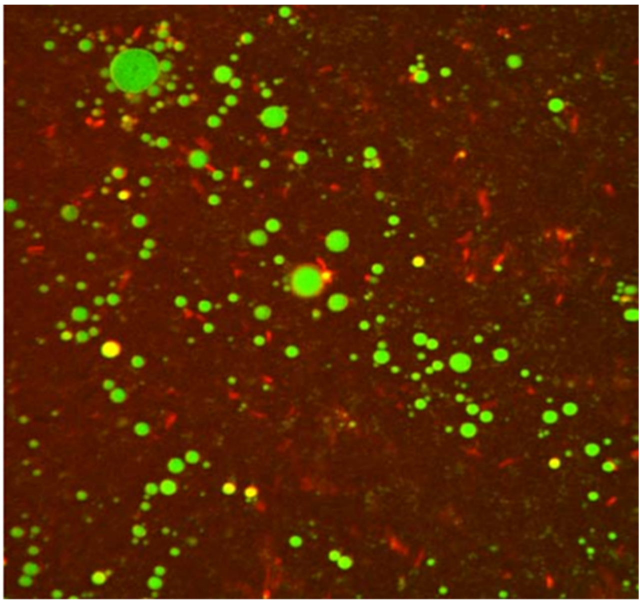


Figure 2. CSLM image of a 10% cottonseed o/w emulsion stabilized by 1% sodium caseinate. (Spherical oil droplets stabilized in the protein network, image size:131 × 131 μm) (produced in NTUA/Laboratory of Food Chemistry and Technology).

The effect of emulsifiers on phenolic antioxidant activities could be also seen from the "angle" of their reported impact on the oil droplet seize. According to Vilasaua et al. [95], the particle size decreases with increasing ionic/nonionic surfactant ratio, up to a certain ratio above which emulsions aggregate. Kiokias et al. [69] reported that in contrast to emulsions stabilized by low molecular weight emulsifiers (Tween 20, SDS), smaller oil droplets, obtained in protein-stabilized emulsions through the increase of protein concentration, were associated with enhanced protection from oxidative changes. Overall, we can claim that the stability of phenolic compounds that are located at the oil-water interface or inside the oil droplets of an o/w emulsion may be affected by droplet size [96]. A decrease in droplet size results in an increase of the oil and interfacial area, where the phenolic compounds can contact free radicals found in the water phase and thus oxidize faster. Additionally, the lipophilic phenolic compounds diffuse faster from the interior of an oil droplet to the exterior as the droplet size decreases [97].

Over the last few years, a number of studies have explored the distribution of phenolics in o/w emulsions by developing pseudophase kinetic models [74,84,98]. The advantage of this approach is that it works on intact emulsions, unlike other methods that require phase separation and cannot provide estimates of the amounts of antioxidants in the interfacial area. Via the use of partition constant values, such models determine the percentages of phenolic acids in the oil, aqueous and interfacial regions of the emulsions. The results of a few studies offer "libraries" of partition constant values for the distribution of various phenolic antioxidants (e.g., CA, 4-hydroxycinnamic acid, di-hydrocaffeic acid, and hydroxytyrosol derivatives) [53,75,99]. Lossada Barreiro et al. [98] investigated the phenolic distributions in intact emulsions by using the pseudo-phase kinetic model and estimated changes in the antioxidant concentration, by using a chemical probe and employing the Schaal oven test. They reported that at any given volume fraction of emulsifier, the concentrations of antioxidants in the interfacial region of stripped corn oil emulsions and their efficiency follow the order: propyl gallates > gallic acid > octylgallates > lauryl gallates. The authors highlighted that these results provide clear evidence that the antioxidant efficiency correlates with its concentration in the interfacial region. Furthermore, Meireles et al. [100] have employed the kinetic method to determine the distribution of a homologous series of chlorogenic acid in olive o/w emulsions. The authors concluded that the activity of chlorogenates in emulsions is greatly dependent on their interfacial concentrations.

The research evidence in o/w emulsions presented in this section (i) notes a clear effect of the type of emulsifier in the interfacial distribution of phenolics, which may vary depending on the mode of their binding interaction; (ii) highlights that the findings of recent kinetic studies (mainly by use of pseudo-phase models) tend to agree how important is the concentration of phenolic compounds in the interfacial region of o/w model emulsion systems in order to interpret their overall antioxidant potential.

3.3. Effect of Polarity on the Antioxidant Activity of Phenolic Compounds

A body of recent research evidence noted that the efficacy of antioxidants in emulsions is highly affected by their polarity [6]. A well-known theory in the field concerns the so-called "polar paradox" which illustrates the paradoxical behavior of antioxidants in different media and rationalizes the fact that polar antioxidants are more effective in less polar media, such as bulk oils, while nonpolar antioxidants are more effective in relatively more polar media, such as o/w emulsions or liposomes [8].

In line with the general concept of this theory, the more polar antioxidants (containing hydrophylic groups) are better distributed in the water phase or the oil-water interface where they may be easily oxidised (in particular under thermally accelerated oxidation conditions). On the other side, the less polar antioxidants (and normally hydrophobic in nature) are preferably located in the lipid core of the emulsion droplets, which is thereby better protected from oxidation [101]. Kanakidi et al. [87] arrived at similar results by highlighting that the more polar RA and carnosic acid, compared to the other phenolic diterpenes, are distributed in the aqueous phase and the oil-water interface where they are faster and promptly oxidized by trace metals or free radicals possibly present there. In the same mode of action, the antioxidant potential of phenolic compounds was reported to decrease with increasing hydrophobicity (e.g., gallic esters less protective than GA) during the oxidative deterioration of bulk oil systems [102]. Noon et al. [103] investigated the efficacy of four natural phenolic antioxidants with varying structures and polarities (quercetin, curcumin, rutin hydrate, and ascorbic acid) against the oxidative deterioration of different o/w emulsion environments. The authors concluded that the most non-polar compounds (curcumin and quercetin) yielded higher peroxide values (PV) reductions (of 65% and 74%, respectively) in 5% oil phase volume emulsions compared to 40% oil phase volume emulsions (just 28% and 43% PV reductions). Another study [74] further demonstrated the applicability of the polar paradox theory in the oxidative stability for n-3 high unsaturated fatty acid-rich water emulsions. While the hydrophilic ascorbic acid acted as a pro-oxidant, natural plant extracts rich in non-polar polyphenols and a-tocopherol presented a strong antioxidant character. Other research studies, though, came out with evidence that is not fully in line with the polar paradox concept. Poyato et al. [5] reported that a *Melissa officinalis* water extract rich in RA was more effective in o/w emulsions and inhibited lipid oxidation more effectively than the lipophilic antioxidant (BHA).

Di Mattia et al. [104] also came out with certain findings that are not in good agreement with the polar paradox theory. The authors reported that GA, although a phenolic compound with a high polarity, exerted a strong antioxidant effect upon its addition to olive o/w emulsions. GA was estimated to be present in the aqueous phase at a much higher (almost double) concentration than the more hydrophobic quercetin under the same experimental interfacial conditions.

Similarly, Bravo-Diaz et al. [105] used gallate and caffeate esters of variable alkyl chain length and hydrophobicity in o/w, Tween 20-based emulsions. The authors reported a decreasing activity with increasing hydrophobicity, which may be attributed to a distributional shifting of the phenolic antioxidants from the interfacial to oil region of the emulsion, based on their increasing oil solubility.

Moreover, Mitrus et al. [14] concluded that GA and its esters tend to accumulate in the interfacial region, and the percentage distributed in the interface increased with hydrophobicity up to a certain length of alkyl chain (called a cut-off effect), due to lack of water solubility of esters with a longer alkyl chain. Costa et al. [7], however, while evaluating the antioxidant efficiency of n-alkyl esters of phenolic compounds in olive o/w emulsions, concluded that the antioxidant distribution in the interface does not correlate directly with the length of the alkyl chain, thereby with the hydrophobicity.

Overall, we should note that various studies in the field do not fully align with polar paradox concepts concerning the antioxidant activity of phenolic compounds in emulsion systems. As a general conclusion, though, the polarity can be a critical factor in moderating the interfacial antioxidant activity as evidenced by recent studies that compare different types of phenolic acids (and other phenolic antioxidants) with varying structure and hydrophobicity in o/w emulsions. For this reason, we also included the next section (Section 3.4) which focuses on the interaction effects of phenolic antioxidants with varying polarities in o/w emulsion systems.

3.4. Synergistic Interfacial Activity of Phenolic Compounds against the Lipid Oxidation of o/w Emulsions

In Section 3.3, polarity was found to determine the phenolic antioxidant activity in various lipid-based systems. As a next step, the potential interaction effect of mixtures of phenolic antioxidants with different degrees of hydrophobicity against the lipid oxidation of o/w emulsions is further discussed. A number of research studies in this scientific field have widely reported over the last decade that more protection against oxidative deterioration of food products is offered through the synergistic action of antioxidants with varying structures, physical properties, and modes of action [106,107]. Filip et al. [108]

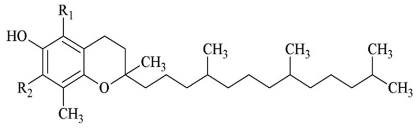
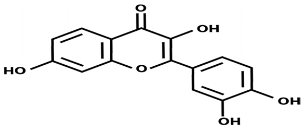
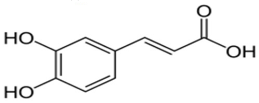
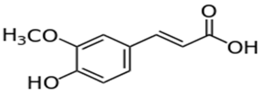
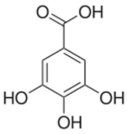
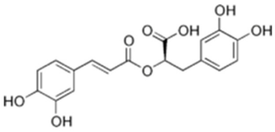
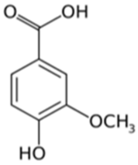
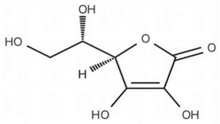
highlighted an enhanced antioxidant activity through the interaction of tocopherols and ascorbic acid in various oil model systems. They claimed that the synergistic effect occurs because of the reduction of tocopherol radicals by ascorbic acid. Zhou and Elias [76] observed a clear protective effect of CA, following its addition in o/w emulsions (stabilised by Tween 20 or Citrem emulsifiers), with tocopherols endogenously present in the oil phase. However, GA acted as a prooxidant accelerating lipid oxidation at the absence of any tocopherols in the emulsion. Wu et al. [108] reported a clear antioxidant character of GA and its alkyl esters when combined with α-tocopherol in o/w emulsions systems. The authors attributed this antioxidant synergy to the initial quick oxidation of α-tocopherol into α-tocopherol quinine, causing its transfer to the interfacial membrane and exposure to oxidation. The tocopherol radicals are reduced back by gallate esters regenerating α-tocopherol in the interfacial layer and enabling antioxidant activity in the emulsion system. Panya et al. [62] noted that the high polarity of RA, and consequently its distribution in the aqueous phase, was responsible for the observed low efficiency in emulsions. The authors reported, however, an enhanced antioxidant effect when RA was combined with α-tocopherol. This could be explained via an increased distribution of RA in the water phase allowing its interaction with the more hydrophobic α-tocopherol on the oil droplet's surface.

Noon et al. [103] found that combinations of ascorbic acid with quercetin or curcumin resulted in antioxidant synergism against the oxidation of o/w emulsions. This research builds on the understanding of the fundamental behaviour of natural antioxidants, such as plant extracts, within different emulsion formulations.

Similarly, Farooq et al. [11] reviewed how polarity and interactions of phenolic antioxidants may determine their antioxidant activity at the oil-water interface of food emulsions. The authors highlighted that synergistic interactions of polar with non-polar phenolics at the oil-water interface may be considered a promising strategy for improving the oxidative stability of emulsions. Further to synergistic activities, we cannot exclude the possibility of some "antagonistic effects between phenolic antioxidants. Liu et al. [109] also referred to the regeneration of α-tocopherol radicals, but this time to clarify antagonistic, rather than synergistic effects, in o/w systems. Following the addition of α-tocopherol at varying concentrations, the authors observed an increased partition of α-tocopherol in an aqueous phase when mixed with γ-oryzanol. They also proposed an inhibitory effect of γ-oryzanol against the regeneration of α-tocopherol. Such antagonism reduced the antioxidant potential of tocopherols in the emulsion system.

The Table 1 below presents an overview of several studies, the results of which have demonstrated a clear protective effect of phenolic compounds (either alone or in combinations) against the oxidative deterioration of o/w emulsions.

Table 1. Overview of literature reporting a clear antioxidant activity of certain phenolic compounds (alone or in combinations) against oxidative deterioration of various model oil-in-water emulsion systems.

Structure	Emulsion Systems/Reported Antioxidant Activities	Literature
α,δ Tocopherols 	Flaxseed o/w emulsions/ Clear effect of tocopherols (δToc > α-Toc)	[30]
Flavonoids (general structure) 	Clear effect of flavonoids in various o/w emulsions (with quercetin being the stronger antitoxidant)/	[34,35,37]
Caffeic acid (CA) 	Tween-based linoleic acid o/w emulsions/clear CA effect	[46]
	Citrem- and Tween-based o/w emulsions/clear CA effect in the presence of endogenous tocopherols	[77]
Ferulic acid (FA) 	Corn oil-based o/w emulsions /clear FA effect	[49]
	Tween-linoleic acid-based emulsions/clear FA effect	[50]
Gallic acid (GA) 	SDS stabilised rapeseed o/w nano-emulsions/clear GA effect	[53]
	Clear effect of GA or its alkyl esters added in combination with α-toc in o/w emulsions	[110]
Rosmarinic acid (RA) 	Tween-based o/w emulsions prepared with linoleic acid or soybean emulsions/clear RA effect	[62]
	Clear effect of RA-rich plant extracts in sunflower o/w emulsions	[19]
Vanillic acid (VA) 	Tween 40-based o/w systems, at pH 3.5/clear effect of VA in the emulsified system	[64]
Ascorbic acid 	Mixtures of ascorbic acid with α-tocopherol in o/w emulsions/strong synergistic antioxidant effect	[108]
	Mixtures of ascorbic acid with quercetin in o/w emulsions/observed synergistic activity	[102]

4. Conclusions

The analysis of literature evidence undertaken in this work has concluded that the well-established antioxidant activity of several phenolic compounds in various o/w emulsion systems is highly dependent on their interfacial distribution. The partition of phenolics within the emulsion phases is a factor that could determine their antioxidant efficiencies in interfacial systems and is influenced by various parameters including pH, emulsifier, and their structure (hydrophilic/hydrophobic character). The highest activity is shown by the phenolic compounds located at the emulsion interface and correlates with their interfacial concentration. In addition, synergistic actions between phenolics have been reported to enhance interfacial antioxidant activity. By monitoring the interfacial distributions of phenolics in o/w emulsions, researchers could further promote their use as functional ingredients in novel food emulsion relevant products (such as various dressings, fresh cheese types, protein-stabilized drinks, etc.). Further work in this field may involve the design of new kinetic studies with the aim to validate and complete the current databases on the distribution constants of various phenolic compounds.

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