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Effect of food structure on the distribution and reactivity of small molecules

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How food structure affects chemical reaction kinetics is one of the big, general problems in food science. We describe how the simple ideas of partitioning and diffusion have been developed to explain increasingly complex behaviors; especially cut-off effects of antioxidants in emulsions and barrier properties of the interface. Finally we consider some ways molecular distribution can be measured.

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The nature of the problem

Almost all foods contain some level of microstructure. Figure 1 shows some examples of a simple mixture of oil, water and surfactant: the oil is present as a droplet stabilized by a monolayer of surfactant, with other surfactant molecules either dissolved as monomers or present as micelles in either phase. The surfactant may also be present in other forms of self-assembled structures, and a lipid bilayer is shown containing some water (i.e., part of a liposome). In some cases, regions of the bulk phases are segregated by the presence of the surfactant structures (e.g., the emulsified lipid droplet is separated from lipids in other droplets while the water inside the liposome is separated from the outside water). Some of these structures are thermodynamically stable while others are kinetically stabilized. Regardless, they are dynamic with molecules constantly diffusing between domains over different timescales.

When small molecules (e.g., antioxidants, antimicrobials, flavors, colors) are added to a structured food, they will partition between phases until they reach their equilibrium distribution; a kinetic process that might not fully resolve within the lifetime of the product. The distribution between phases means their local concentration is not the same as the concentration added and therefore their reactivity is changed. For example, if two compounds were highly reactive with one another but one was dissolved in the oil phase while the other was dissolved in the water phase, they would only react slowly if at all. This partitioning model has been used to explain how food structure affects the reactivity of antimicrobials [1,2], flavors [3,4] and especially antioxidants [5,6]. The essence of the problem does not change if we add more complexity to Figure 1 to better approximate a real food. Indeed, depending on the nature of the structures selected, Figure 1 can start to resemble a living cell where the same rules of partitioning and diffusion will determine the biological reactivity of drugs [7,8].

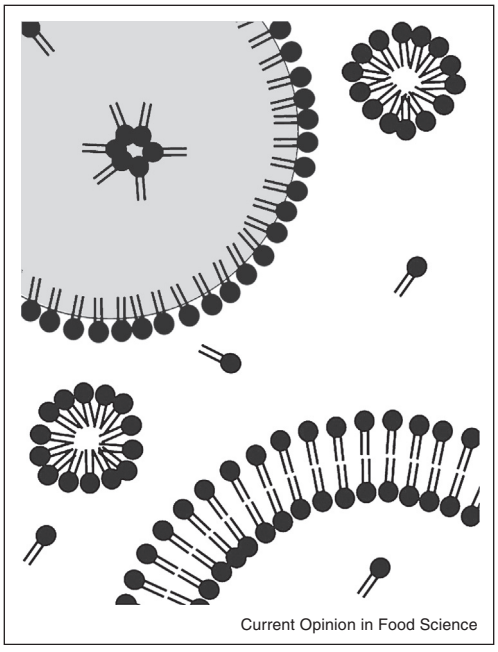
In this short review, we will consider the broad problem of ingredient partitioning and reactivity in foods and related biological systems.

Partitioning of antioxidants: polar paradox and cut-off

The effectiveness of antioxidants have long been known to be dependent on food microstructure and Porter [9,10] provided the first general rule: polar antioxidants perform better in bulk lipids while non-polar antioxidants perform better in aqueous systems (i.e., micelles, liposomes, emulsions). The physical mechanism proposed for this so called 'polar paradox' was that the effective antioxidants were concentrated in the regions of the system most vulnerable to oxidation, typically interfaces [11]. However, there has been some debate since then as to which interfaces are the most relevant [12••,13••]. In many bulk lipids, polar lipids form self-assembled colloids [14] that may incorporate small amounts of water and, in some cases, serve as catalytic centers for oxidation [15]. If the antioxidants can effectively interact with these structures, they appear to perform better, although a clear, predictive model is yet to be established [13••]. In emulsions on the other hand, the oil–water interface is believed to be critical.

One approach to studying antioxidant distribution is the use of homologous series of fatty acid esters of a polar antioxidant. Differences in the rates of lipid oxidation are therefore due to systematic differences in partitioning behavior alone as the reactive group is unchanged. In studies with lipophilized antioxidants in emulsions, the

Figure 1



Highly schematic diagram of some lipid structures possible in a food. Water is shown white, while lipid is slightly shaded.

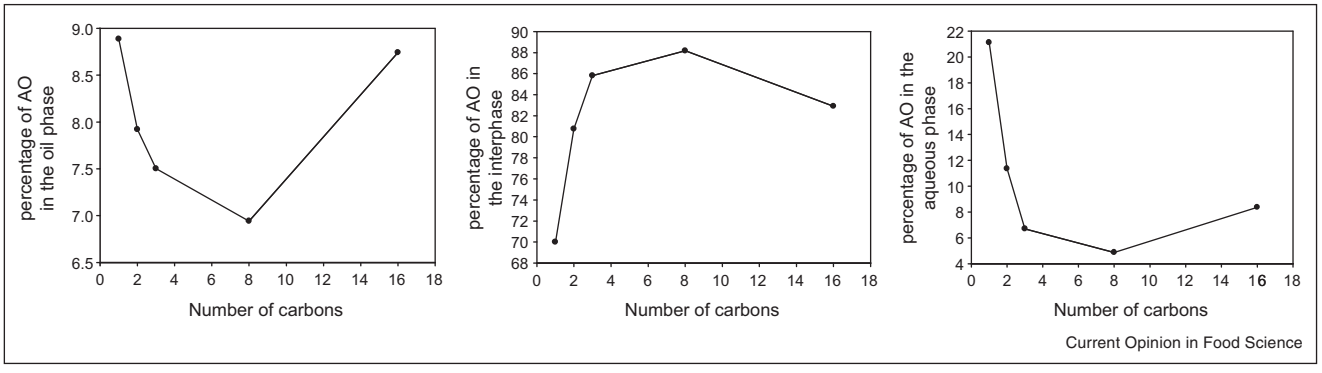
effectiveness of antioxidants has been shown to increase as a function of increasing fatty acid chain length to a critical point, but then to dramatically decrease beyond that point. For example the optimum chain length for lipophilized caffeic acid derivatives in o/w emulsions was C8 [16••] and in a similar studies with fatty acid esters of rosmarinic acid [17] and chlorogenic acid [18••] the optimum chain length was C8 and C12 respectively. Cut-off effects have also been observed in fish oil emulsions for various lipophilized organic acids [19,20].

The increase in antioxidant activity with moderate lipophilization can be explained by an increase in antioxidant concentration at the interface where they are most effective. Laguerre and others [18••] propose three molecular mechanisms for the sudden decrease in antioxidant effectiveness, the so-called 'cut-off effect', in more highly lipophilized compounds. First, a reduction in molecular mobility at higher molecular weight slows reactivity. However, the modest incremental change in molecular weight (~38%) going from the most effective C8 derivative of caffeic acid to the almost ineffective C16 does not seem adequate to fully explain the sudden change in reactivity. A second proposed mechanism for the cut-off is that the longer carbon chain positions the antioxidants toward the center of droplet or the core of the micelle, where they are less effective. Indeed, the optimum antioxidant efficiency at caffeic acid (C8) when the interfacial concentration was highest (Figure 2, [16••]). As the chain length was increased beyond the limit, the amount in the surfactant phase decreased and the amount in the lipid phase and aqueous phase increased. The increase in the lipid phase is consistent with the internalization theory and the increase in the aqueous phase is consistent with the third mechanism: beyond the critical chain length, antioxidants may form aggregates (micelles or precipitates), thus reducing their concentration in the reactive phase or slowing their rate of diffusion between phases. This theory seems reasonable, particularly if a highly lipophilic antioxidant is added to an aqueous lipid dispersion phase in an ethanolic solution. As the ethanol is suddenly diluted, the antioxidant may precipitate before it reaches the lipid phase (i.e., 'the ouzo effect') and only slowly diffuses from there to reach equilibrium distribution. One would expect different results if the highly non-polar antioxidant was initially dissolved in the lipid. Whatever the exact reason, it is notable that while the polar paradox presumes partitioning between two domains, two of the three cut-off mechanisms the presence of a third.

Biological implications of the cut-off effect

Many diseases are associated with the development of reactive oxygen species; so using lipophilization to target

Figure 2



Distribution of caffeic acid fatty acid esters between phases in a 4:6 olive oil:water emulsion. Optimum antioxidant activity was seen for the C8 ester. Calculated from the data presented in Ref. [16••].