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Ability of Surfactant Micelles to Alter the Partitioning of Phenolic Antioxidants in Oil-in-Water Emulsions

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In oil-in-water emulsions, the physical location of antioxidants can be an important determinant in their activity. Surfactants can potentially influence the physical location of antioxidants in oil-in-water emulsions by causing solubilization of lipid-soluble antioxidants into the aqueous phase. Excess Brij micelles in an oil-in-water emulsion were found to increase the partitioning of phenolics into the continuous phase with polar antioxidants (propyl gallate) partitioning more than nonpolar antioxidants (butylated hydroxyltoluene). Solubilization of propyl gallate was rapid coming to equilibrium in less than 5 min. Increasing surfactant micelle concentrations from 0.3 to 2.8% increased the solubilization of propyl gallate by 2.3-fold. Solubilization of phenolic antioxidants into the aqueous phase by Brij micelles did not alter the oxidative stability of salmon oil-in-water emulsions, suggesting that surfactant micelles influenced oxidation rates by mechanisms other than antioxidant solubilization.

KEYWORDS: Lipid oxidation, fish oil, antioxidants, emulsions, surfactants, solubilization

INTRODUCTION

In most processed foods, lipids are found as oil-in-water or water-in-oil emulsions (*1*, *2*). In foods, these emulsions are stabilized by surface-active agents such as proteins, fatty acids, and esters of polyoxyethylene (e.g., Tweens). The oxidation of emulsified lipids is mechanistically different than bulk oils due to the properties of the emulsion droplet interface and the ability of prooxidants, antioxidants and oxidizable substrates to partition into the oil, interface, and water phases of the emulsion (for review see ref *3*). The properties of the emulsion droplet interface influences lipid oxidation due to its ability to attract/repel prooxidants and antioxidants and by forming a physical barrier that alters interactions between lipids and water-soluble prooxidants (*4*−*12*).

The influence of the physical partitioning of antioxidants in oil-in-water emulsions on lipid oxidation has been the focus of numerous research projects in the past decade (*8*−*12*). In oil-in-water emulsions, the partitioning behavior of an antioxidant can have a marked effect on its reactivity. In general, nonpolar antioxidants that are retained in emulsion droplets are more effective inhibitors of lipid oxidation than polar antioxidants that have significant partitioning into the continuous phase of an oil-in-water emulsion. Partitioning of antioxidants in oil-in-water emulsions is influenced by their molecular characteristics (e.g., polarity, molecular weight, and surface activity). However, emulsifiers could also play an important role in antioxidant partitioning since they can aid in the solubilization of nonpolar compounds out of the lipid into the water phase (*13*, *14*).

Many oil-in-water emulsions contain more surfactant than is needed to completely saturate the emulsion droplet surface, which results in the formation of surfactant micelles in the continuous phase. These surfactant micelles are capable of solubilizing components of the lipid droplets into the water phase (*15*), a process that is dependent on both surfactant type and concentration (*16*). Many types of surfactant micelles are not very effective at solubilizing triacylglycerols because the dimensions of their hydrophobic core is too small to accommodate these relatively large, bulky lipid molecules (*17*). On the other hand, surfactant micelles can solubilize appreciable amounts of smaller lipids such as hydrocarbons (*15*, *16*). Chain-breaking antioxidants (e.g., phenolics) contain varying degrees of surface activity due to their differences in polarity. The surface activity of phenolics has been suggested to result in their partitioning into the emulsion droplet interface (*10*). Therefore, it is possible that phenolic antioxidants could be removed from emulsion droplets by surfactant solubilization thereby altering the oxidative stability of oil-in-water emulsions. Only small changes in antioxidant partitioning out of the emulsion droplet could increase oxidation rates since small concentrations of antioxidants (50−1,000 ppm of oil content) are normally used in foods (*12*).

The objective of this research was to determine the ability of surfactant micelles to alter the partitioning properties of phenolic antioxidants in oil-in-water emulsions. The ability of surfactant micelles to solubilize phenolic antioxidants from lipid

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droplets and the effects of antioxidant solubilization on lipid oxidation rates was determined.

MATERIALS

Olive oil was purchased from a local retail outlet. To obtain fresh salmon oil, salmon fillets (purchased from a local retailer) were hand-chopped into small pieces and minced for 3 min in a food processor. The mince was then centrifuged at 10 000 rpm for 20 min, and the resulting lipid was decanted and stored at −80 °C until use. The isolated salmon oil consisted of 99.5 ± 0.2% triacylglycerol (*18*). The levels of oxidation products in the oil was 0.32 mmol of lipid peroxides/kg of oil (as determined by the method of Shantha and Decker, *19*) and 0.04 mmol of TBA-reactive substances/kg of oil (as determined by the method of McDonald and Hultin, *20*). All other reagents including phenolic antioxidants and surfactants were obtained from Sigma Chemical Company (St. Louis, MO).

METHODS

Emulsion Preparation. Emulsions were prepared by mixing 10% lipid (olive oil, salmon oil, or hexadecane) into a solution containing 1% Brij 700 and 10 mM of both acetate and imidazole buffers at pH 3.0. Coarse emulsions were prepared by homogenizing the mixture with a Brinkman PT 10/35 Polytron (Westbury, NY) at a speed setting of 7 for 1 min. The coarse emulsions were then sonicated with a Braun-Sonic U (B. Braun Biotech, Allentown, Pa.) at 4 °C for 4−6 min at a power setting of + 300 and 0.5 duty cycle to obtain the desired particle size. The final emulsion droplet diameter ranged from 0.3 to 0.4 μm as determined by laser light scattering (Horiba LA-900; Horiba Instruments, Irving, CA; 5). The phenolic antioxidants, propyl gallate (PG), tertiary butylhydroquinone (TBHQ), and butylated hydroxyltoluene (BHT) were added to the lipid using a methanol carrier. The methanol was then evaporated from the lipid with nitrogen at room temperature prior to emulsification. Phenolic antioxidants were added over the concentration range of 0−400 ppm of the lipid content. Ethylenediaminetetraacetic acid (100 μM) was added to the buffer in antioxidant partitioning experiments to minimize oxidation of the antioxidants and lipids. After preparation of the emulsions, surfactant micelles were incorporated into the continuous phase of the emulsion by adding varying concentrations of the desired surfactants in acetate/imidazole buffer to give a final lipid concentration of 5%.

Measurement of Antioxidant Partitioning. To determine the concentration of surfactant and antioxidants in the continuous phase, the emulsion was centrifuged at 10000*g* for 35 min at 10 °C in a Sorvall RC2-B refrigerated centrifuge. The continuous phase (3 mL) from the lower layer of the centrifuge tube was removed with a syringe. Surfactant concentrations in the continuous phase were determined using high precision density measurements. Samples were first degassed for 15 min at 25 °C. The density of the degassed samples were then determined in a Mettler Toledo DE50 oscillating U-tube density meter and surfactant concentrations were determined from a calibration curve constructed with solutions containing known amounts of surfactant. Phenolic concentrations in the continuous phase were determined using the Folin-Ciocalteu method according to Eguchi et al. (*21*) with 120 μL of the 50% Folin-Ciocalteu reagent being added to 2 mL of continuous phase. Absorbance at 725 nm was measured immediately after addition of Folin-Ciocalteu reagent (to correct for sample turbidity if present) and again after 60 min of incubation at room temperature in the dark. Concentrations were determined from standard curves of PG, TBHQ, and BHT. Addition of surfactant micelles to the standard curve samples showed that the presence of surfactant micelles did not interfere with the Folin-Ciocalteu reaction.

Measurement of Lipid Oxidation. The influence of phenolic antioxidant solubilization by surfactant micelles on lipid oxidation was determined in salmon oil-in-water emulsions at pH 3.0 and 32 °C. Emulsions were prepared with and without TBHQ, and oxidation was monitored with lipid hydroperoxides and headspace propanal (*6*). Lipid hydroperoxides in the emulsions were extracted by adding 0.3 mL of the emulsion to 1.5 mL of isooctane/isopropanal (3:2; v/v), followed by vortexing three times for 10 s each. After centrifugation for 2 min at 2000*g*, 0.2 mL of the clear upper solvent layer was collected, and lipid hydroperoxides were quantitated using a modified method of Shantha and Decker (*19*). The sample extract (0.2 mL) was mixed with 2.8 mL of methanol/1-butanol (2:1; v/v) and 30 μL of thiocyanate/Fe^{2+} solution and then vortexed. The thiocyanate/Fe^{2+} solution was made by mixing one part 3.94 M thiocyanate solution with one part 0.072 M Fe^{2+} solution (obtained from the supernatant of a mixture of 1 part 0.144 M $FeSO_4$ and 1 part 0.132 M $BaCl_2$ in 0.4 M HCl). After 20 min of incubation at room temperature, absorbance was measured at 510 nm. Lipid hydroperoxide concentrations were determined using a cumene hydroperoxide standard curve.

Propanal concentrations in the salmon oil emulsions were determined by placing 1.0 mL of the emulsion samples in 10-mL headspace vials that were then sealed with poly(tetrafluoroethylene)/butyl rubber septa using a crimper and aluminum seals. Headspace propanal was determined using a Hewlett-Packard (HP) 5890 gas chromatograph (Avondale, PA) with a HP 19395A headspace sampler and coupled to a HP 3392A integrator. The headspace conditions were as follows: sample temperature, 40 °C; equilibration time, 5 min; splitless injector temperature, 180 °C; oven temperature, 70 °C; detector temperature, 200 °C. The aldehydes were separated on a HP methyl silicone (DB-1) fused silica capillary column (50 m, 0.31 mm i.d., 1.03 μm film thickness). Concentrations were determined from peak areas using a standard curve made from authentic propanal since it was determined that the surfactant micelles did not influence the amount of propanal partitioning into the headspace.

RESULTS AND DISCUSSION

Final emulsions contained 0.5% Brij 700 and 5% hexadecane, olive oil, or salmon oil. Under the emulsification conditions used, the hexadecane, olive oil, and salmon oil-in-water emulsions contained from 0.05 to 0.15% (average 0.07%), 0.19−0.32% (average 0.25%), and 0.32−0.34% (average 0.31%) surfactant in the continuous phase, respectively (**Table 1**). Since the polarity of oils increases with increasing degree of unsaturation (*22*), polarity of these different oil phases would be expected to be in the order of hexadecane < olive oil ≤ salmon oil. The lower amount of continuous phase surfactant in the hexadecane emulsion could be due to the lower polarity of the hexadecane that would result in greater association of the surfactant with the oil phase. However, unlike hexadecane, olive and salmon oil would be expected to contain polar lipids (e.g., fatty acids and monoacylglycerols), which may partition into the continuous phase or may displace Brij 700 from the emulsion droplet interface and thereby could be responsible for increasing continuous phase surfactant concentrations. As expected, addition of Brij 700 to the emulsions increased continuous phase surfactant concentrations 1.04−1.20% and 2.51−2.73% for 1 and 2.5% added Brij 700, respectively (**Table 1**).

Added Brij 700 was able to increase the partitioning of propyl gallate into the continuous phase in a rapid, concentration-dependent manner. **Figure 1** shows that the partitioning of propyl gallate into the continuous phase by Brij 700 was complete after 5 min of incubation (first sampling time). This is in contrast to other lipids such as hexadecane that takes 5 days to be completely solubilized by Tween 20 micelles and triacylglycerols from corn oil that were not solubilized by Tween 20 micelles after 14 days of storage (*17*). Differences in the solubilization rates between propyl gallate, hexadecane, and triacylglycerols is likely due to differences in molecular polarity, size, and geometry with the smaller, more polar propyl gallate being more easily incorporated into the surfactant micelles. Increasing continuous phase Brij 700 concentrations increased the solubilization of propyl gallate with addition of 0.5−4.5% Brij 700 into the continuous phase causing a 3- to 13-fold increase in continuous phase propyl gallate concentrations as compared to the no added surfactant control (**Figure 2**).

Table 1. Continuous Phase Brij 700, Propyl Gallate, Tertiary Butylhydroquinone (TBHQ), and Butylated Hydroxytoluene Concentrations in 5% Hexadecane, Olive Oil, or Salmon Oil-in-Water Emulsions[a]

		hexadecane emulsions		olive oil emulsions		salmon oil emulsions	
antioxidant	% added surfactant in sample	% surfactant in continuous phase	phenolic content in continuous phase (ppm)	% surfactant in continuous phase	phenolic content in continuous phase (ppm)	% surfactant in continuous phase	phenolic content in continuous phase (ppm)
control	0.0	0.05	0.0	0.21 ± 0.08	0.79 ± 0.00	0.34 ± 0.06	0.07 ± 0.15
	1.0	1.18	0.0	1.04 ± 0.04	1.12 ± 0.44	n.d.	n.d.
	2.5	2.74	0.0	2.58 ± 0.01	1.38 ± 0.01	2.84 ± 0.14	1.43 ± 0.31
propyl gallate (20 ppm in emulsion)	0.0	0.11	0.55 ± 0.06	0.32 ± 0.11	5.35 ± 0.09	n.d.	n.d.
	1.0	1.17	4.03 ± 0.07	1.17 ± 0.03	9.07 ± 0.23	n.d.	n.d.
	2.5	2.72	6.86 ± 0.09	2.79 ± 0.08	12.48 ± 0.00	n.d.	n.d.
TBHQ (20 ppm in emulsion)	0.0	0.05	0.03 ± 0.02	0.19 ± 0.02	2.59 ± 0.09	0.32 ± 0.02	5.37 ± 0.71
	1.0	1.19	1.43 ± 0.03	1.12 ± 0.05	6.10 ± 0.16	n.d.	n.d.
	2.5	2.75	4.26 ± 0.03	2.51 ± 0.03	9.26 ± 0.12	2.88 ± 0.12	13.50 ± 0.47
BHT (20 ppm in emulsion)	0.0	0.05	0.05 ± 0.02	0.24 ± 0.02	0.40 ± 0.07	n.d.	n.d.
	1.0	1.20	0.35 ± 0.25	1.13 ± 0.05	1.43 ± 0.08	n.d.	n.d.
	2.5	2.73	1.32 ± 0.16	2.76 ± 0.09	1.96 ± 0.15	n.d.	n.d.

[a] n.d. = not determined

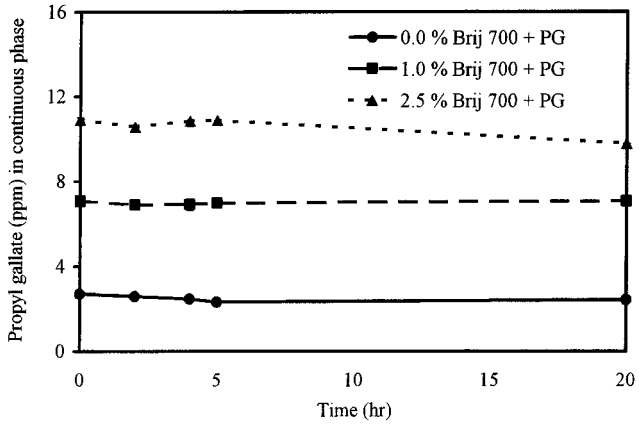

Figure 1. Solubilization of propyl gallate (PG) from olive oil (5%)-in-water emulsions by continuous phase Brij 700 as a function of time. PG concentrations calculated as total phenolics in the presence of added PG − total phenolics in the absence of added PG.

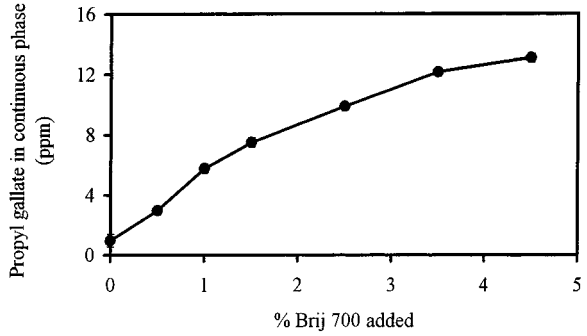

Figure 2. Solubilization of propyl gallate (PG) from olive oil (5%)-in-water emulsions as a function of continuous phase Brij 700 concentrations (0–4.5%).

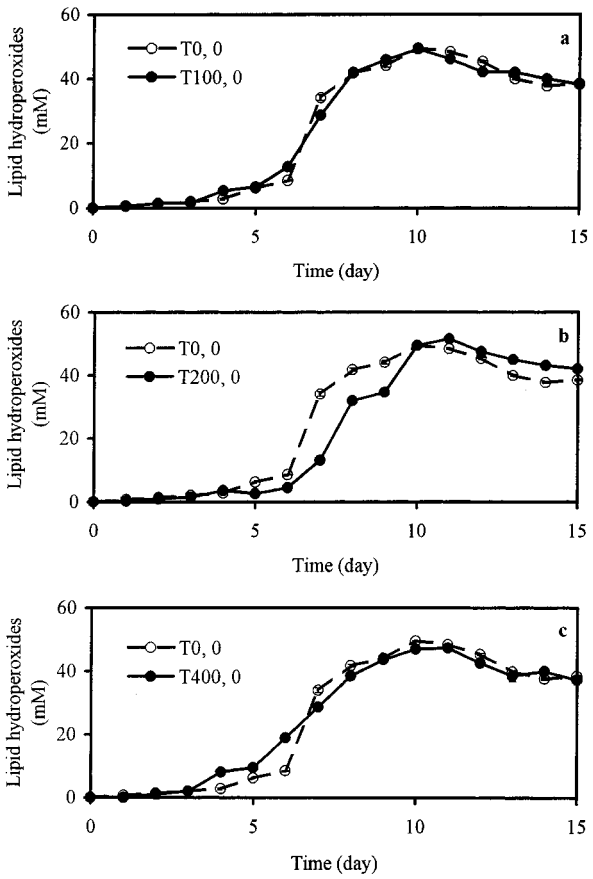

Figure 3. Formation of lipid hydroperoxides in salmon oil-in-water emulsions containing no added Brij 700 in the continuous phase. Emulsions were made without TBHQ and no added Brij 700 (T0, 0), with 100 ppm TBHQ and no added Brij 700 (T100, 0), with 200 ppm TBHQ and no added Brij 700 (T200, 0), and with 400 ppm TBHQ and no added Brij 700 (T400, 0).

The solubilizing activity of Brij 700 micelles (0−2.5%) was also dependent on phenolic polarity with solubilization in the hexadecane-in-water emulsion system being in the order of PG (2.6−32%) > TBHQ (0.2−20%) > BHT (0.2−6%) (**Table 1**). It would be expected that PG with its three hydroxyl groups would be more surface active than TBHQ and BHT with their two and one hydroxyl groups, respectively. Greater surface activity would result in a larger proportion of the phenolic at the emulsion droplet interface meaning that it could be solubilized into surfactant micelles more effectively. In olive oil-in-water emulsions similar patterns in the effect of phenolic polarity on solubilization were observed (**Table 1**). However, in olive oil as well as in salmon oil-in-water emulsions, greater amounts of antioxidant were observed to be solubilized in the continuous phase as compared to hexadecane-in-water emulsions. For example, in the presence of 2.5% added Brij 700, TBHQ concentrations in the continuous phase were 20, 44, and 64% for hexadecane, olive oil, and salmon oil emulsions,

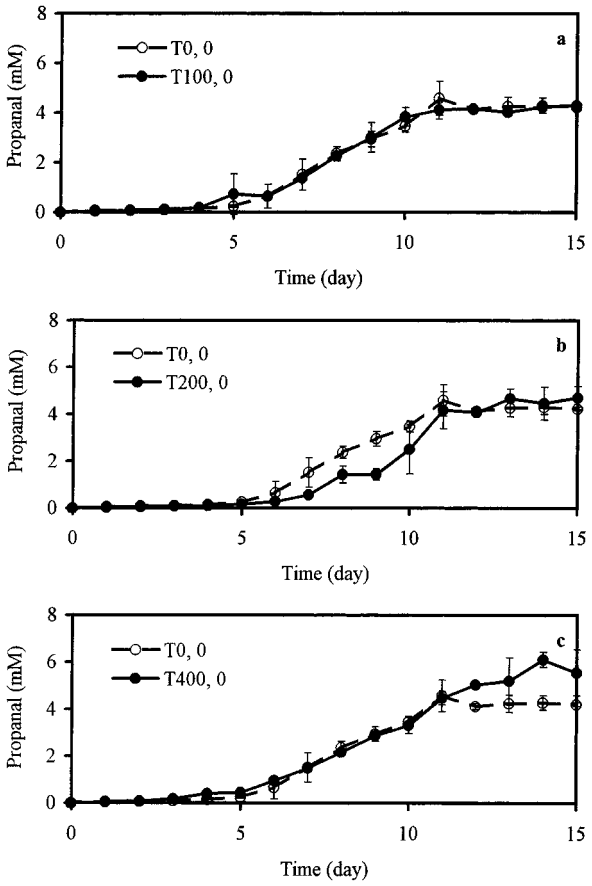

Figure 4. Formation of headspace propanal in salmon oil-in-water emulsions containing no added Brij 700 in the continuous phase. Emulsions were made without TBHQ and no added Brij 700 (T0, 0), with 100 ppm TBHQ and no added Brij 700 (T100, 0), with 200 ppm TBHQ and no added Brij 700 (T200, 0), and with 400 ppm TBHQ and no added Brij 700 (T400, 0).

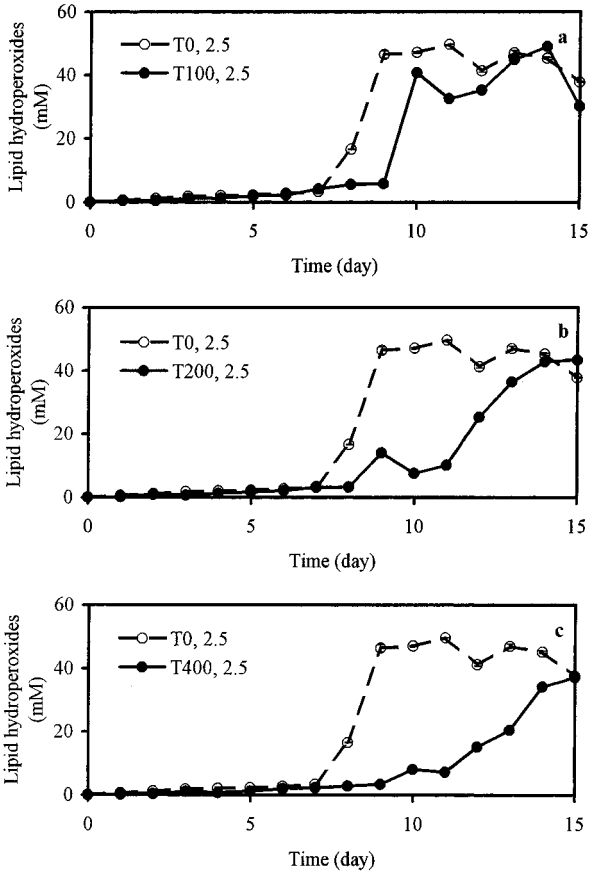

Figure 5. Formation of lipid hydroperoxides in salmon oil-in-water emulsions containing 2.5% added Brij 700 in the continuous phase. Emulsions were made without TBHQ and 2.5% added Brij 700 (T0, 2.5), with 100 ppm TBHQ and 2.5% added Brij 700 (T100, 2.5), with 200 ppm TBHQ and 2.5% added Brij 700 (T200, 2.5), and with 400 ppm TBHQ and 2.5% added Brij 700 (T400, 2.5).

respectively. The differences were not due to the solubilization of other endogenous phenolics from the food oils because less than 6.5 μmol of phenolics/kg of emulsion were solubilized in oil and salmon oil emulsions with no added phenolics. The solubilization of more of the added phenolics in the food oils was somewhat surprising since it was expected that as the oil became more polar (salmon oil > olive oil > hexadecane), the antioxidants would exhibit lower surface activity and thus would have higher retention in the oil droplet. However, it is likely that the olive and salmon oil would contain surface active material such as free fatty acids, mono and diacylglycerols, and phospholipids. These surface-active compounds could cause displacement of the phenolics from the emulsion droplet interface thus causing increased continuous phase concentrations in the presence of surfactant micelles. While phenolic solubilization was greatly influenced by surfactant concentrations, it was not influenced by phenolic concentrations. In the presence of 1.0% added Brij 700 and 100−400 ppm TBHQ, continuous phase TBHQ concentrations increased, showing that the micelles had the capacity to solubilize more TBHQ (data not shown).

To determine if surfactant solubilization of phenolic antioxidants impacted the oxidative stability of oil-in-water emulsions, salmon oil-in-water emulsions were prepared with and without TBHQ and lipid oxidation was monitored by measuring lipid hydroperoxides and headspace propanal. In the presence of no added Brij 700 surfactant micelles, only 200 ppm of TBHQ was found to inhibit lipid oxidation as determined by both hydroperoxides and headspace propanal (**Figures 3** and **4**). At 100 ppm, TBHQ concentration may not have been high enough to control oxidation, while 400 ppm TBHQ may not have inhibited lipid oxidation due to the ability of phenolic antioxidants to exhibit prooxidant activity at high concentrations (*12*). In the presence of 2.5% added Brij 700, the antioxidant activity of TBHQ changed dramatically with all TBHQ concentrations inhibiting both lipid hydroperoxide and propanal formation (**Figures 5** and **6**). This increase in antioxidant activity occurred despite the fact that the added Brij 700 would decrease TBHQ concentrations in the salmon oil emulsion droplets. For example, predicted emulsion droplet TBHQ concentrations in the presence of no added Brij 700 would be 72 ppm in emulsions to which 100 ppm of TBHQ had been added. This compares to a predicted emulsion droplet TBHQ concentration of 80 ppm in the presence of 200 ppm added TBHQ at 2.5% added Brij 700. Despite the similarities in emulsion droplet TBHQ concentrations in these two systems, the antioxidant activity was much greater in the system with the additional 2.5% Brij 700.

The greater antioxidant activity of TBHQ in the presence of high surfactant micelle concentrations may be partially due to the slower lipid oxidation rates observed in the 2.5% added Brij 700 emulsion system. The lag phase for hydroperoxide and headspace propanal formation were approximately 5 days for no added Brij 700 and 8 days for 2.5% added Brij 700, respectively (**Figures 3**−**6**). Previous work has shown that Brij surfactants do not have substantial free radical scavenging

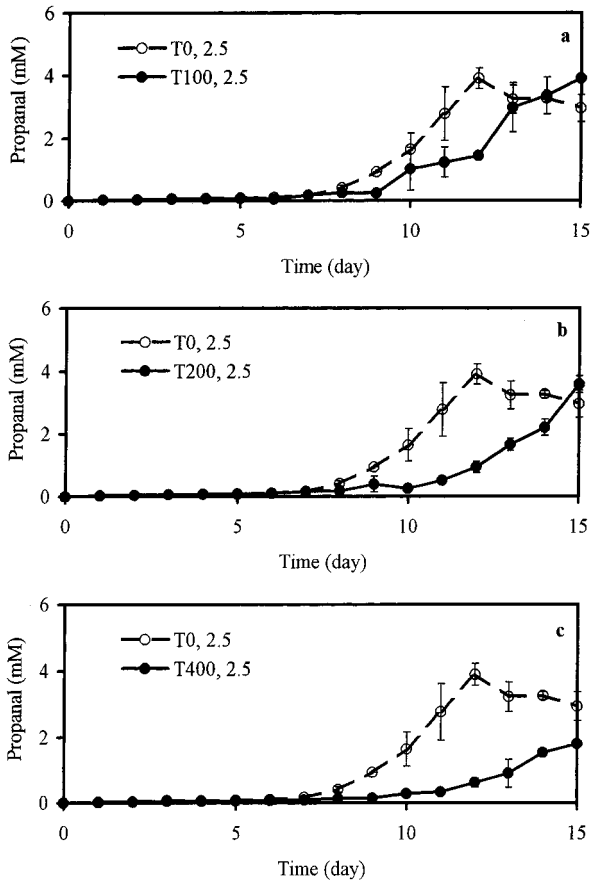

Figure 6. Formation of headspace propanal in salmon oil-in-water emulsions containing 2.5% added Brij 700 in the continuous phase.. Emulsions were made without TBHQ and 2.5% added Brij 700 (T0, 2.5), with 100 ppm TBHQ and 2.5% added Brij 700 (T100, 2.5), with 200 ppm TBHQ and 2.5% added Brij 700 (T200, 2.5), and with 400 ppm TBHQ and 2.5% added Brij 700 (T400, 2.5).

activity (*23*). Lipid oxidation in oil-in-water emulsions is highly dependent on iron promoted decomposition of hydroperoxides into free radicals (for review see ref *3*). It is possible that the Brij micelles could be inhibiting lipid oxidation by causing partitioning of surface-active lipid hydroperoxides out of the emulsion droplets where they would be less likely to produce free radicals that could attack the unsaturated fatty acids in the interior of the emulsion droplet. Likewise, the Brij micelles could also be solubilizing transition metals such as iron causing their partitioning away from the emulsion droplet thereby decreasing their reactivity. Either or both of these factors could decrease free radical production in emulsions. If free radical production was reduced, this would decrease TBHQ oxidation rates, thus providing more antioxidant to inhibit lipid oxidation. It may also be possible that the Brij micelles could be influencing the activity of the TBHQ. In the presence of high concentrations of continuous phase Brij micelles, a substantial proportion of TBHQ would reside outside of the emulsion droplet in surfactant micelles. This continuous phase antioxidant pool could exchange with the TBHQ in the emulsion droplets thus providing a source of unoxidized antioxidant.

CONCLUSIONS

The presence of excess surfactant in the continuous phase of an oil-in-water emulsion can have dramatic effects on the physical location of phenolic antioxidants. Surfactant micelles were able to rapidly (<5 min) partition propyl gallate out of emulsion droplets with increasing surfactant increasing the amount of phenolic in the continuous phase. Polarity influenced phenolic solubilization by surfactant micelles with the nonpolar antioxidant BHT being solubilized less than the more polar antioxidants TBHQ and propyl gallate. While surfactant micelles were capable of increasing the partitioning of antioxidants out of emulsion droplets, they did not cause a decrease in antioxidant effectiveness. This was likely due to the ability of the surfactant micelles to inhibit oxidation by themselves, a factor which would spare antioxidants from oxidation and potentially increase their effectiveness.

Antioxidants are often reported to have varying degrees of activity in different food and model systems. While the level of surfactant used in these experiments is greater than would be expected in foods, this research does provide important information that may help to explain some of these reported differences in antioxidant activity since emulsion systems often have varying degrees of surface active materials which may form micelles and cause partitioning of antioxidants, prooxidants and oxidizable substrates (e.g., lipid hydroperoxides). The observation that the partitioning of nonpolar antioxidants such as BHT are not strongly influenced by surfactant micelles may also help to explain why nonpolar antioxidants are consistently more effective than polar antioxidants in oil-in-water emulsion.

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LITERATURE CITED

(1) McClements, D. J. *Food Emulsions: Principles, Practice, and Techniques*; CRC Press: Boca Raton, FL, 1999.
(2) Friberg, S. E.; Larsson, K. *Food Emulsions,* pp 139−147. Marcel Dekker: New York, . 1997.
(3) McClements, D. J.; Decker, E. A. Lipid oxidation in oil-in-water emulsions: Impact of molecular environment on chemical reactions in heterogeneous food systems. *J. Food Sci.* **2000**, *65*, 1270−1282.
(4) Mei, L.; McClements, D. J.; Wu, J.; Decker, E. A. Iron-catalyzed lipid oxidation in emulsions as affected by surfactant, pH and NaCl. *Food Chem.* **1998**, 61, 307−312.
(5) Mancuso, J. R.; McClements, D. J.; Decker, E. A. The effects of surfactant type, pH, and chelators on the oxidation of salmon oil-in-water emulsions. *J. Agric. Food Chem.* **1999**, *47*, 4112−4116.
(6) Silvestre, M. P. C., Chaiyasit, W., Brannan, R. G., McClements, D. J., Decker, E. A. Ability of Surfactant Headgroup Size to Alter Lipid and Antioxidant Oxidation in Oil-in-Water Emulsions. *J. Agric. Food Chem.* **2000**, *48*, 2057−2061.
(7) Chaiyasit, W., Silvestre, M. P. C., McClements, D. J., and Decker, E. A. Ability of surfactant tail group size to alter lipid oxidation in oil-in-water emulsions. *J. Agric. Food Chem.* **2000**, *48*, 3077−3080.
(8) Huang, S.-W., Frankel, E. N., Schwarz, K., Aeschbach, R., German, J. B. Antioxidant activity of carnosic acid and methyl carnosate in bulk oils and oil-in-water emulsions *J. Agric. Food Chem.* **1996**, *44*, 2951−2956.
(9) Huang, S.-W., Hopia, A., Schwarz, K., Frankel, E. N., German, J. B. Antioxidant activity of α-tocopherol and Trolox in different lipid substrates: Bulk oils vs oil-in-water emulsions. *J. Agric. Food Chem.* **1996**, *44*, 444−452.
(10) Huang, S.-W.; Frankel, E. N.; Aeschbach, R.; German, J. B. Partition of selected antioxidants in corn oil−water model systems. *J. Agri. Food Chem.* **1997**, 45, 1992−1994.
(11) Frankel, E. N.; Huang, S. W.; Kanner, J.; German, J. B. Interfacial Phenomena in the Evaluation of Antioxidants − Bulk Oils Vs Emulsions. *J. Agric. Food Chem.* **1994**, *42*, 1054−1059.

(12) Frankel, E. N. *Lipid Oxidation*, pp 139−147. The Oily Press: Dundee, Scotland. 1998.
(13) Shinoda, K.; Friberg, S. *Emulsions and Solubilization*; Wiley-Interscience: New York, NY, 1986.
(14) Elworthy, P. H.; Florence, A. T.; Macfarlane, C. B. *Solubilization by surface active agents and its application in chemistry and biological sciences*, Chapman and Hall: London, UK, 1968.
(15) McClements, D. J. and Dungan, S. R. Light scattering study of solubilization of emulsion droplets by nonionic surfactants. *Colloids Surfs. A.* **1995,** *104*, 127−132.
(16) Weiss, J.; Coupland, J. N.; McClements, D. J. Solubilization of hydrocarbon droplets suspended in an nonionic surfactant solution. *J. Phys. Chem.* **1996**, *100*, 1066−1071.
(17) Coupland, J. N., Weiss, J., Lovy, A., and McClements, D. J. Comparison of the solubilization kinetics of triacylglycerol and hydrocarbon emulsion droplets in a micellular solution. *J. Food Sci.* **1996**, *61*, 1114−1117.
(18) Mei, L. Y.; Decker, E. A.; McClements, D. J. Evidence of iron association with emulsion droplets and its impact on lipid oxidation. *J. Agric. Food Chem.* **1998**, *46*, 5072−5077.
(19) Shantha, N. C.; Decker, E. A. Rapid, sensitive, iron-based spectrophotometric methods for determination of peroxides values of food lipids. *J. AOAC Int.* **1994**, *77*, 421−424.
(20) McDonald, R. E.; Hultin, H. O. Some characteristics of the enzymic lipid
(21) peroxidation systems in the microsomal fraction of flounder muscle. *J. Food Sci.* **1987**, 52, 15−21, 27.
(22) Eguchi, Y., Curtis, O. F. and Shetty, K. Interaction of hyperhydricity-preventing *Pseudomonas* sp. with oregano (*Origanum vulgare*) and selection of high phenolics and rosmarinic acid-producing clonal lines. *Food Biotech.* **1996**, *10*, 191−202.
(23) Swern, D. *Bailey's Industrial Oil and Fat Products*, Vol. 1; Wiley-Interscience: New York, 1979; p 227.
(24) Mancuso, J. R.; McClements, D. J.; Decker, E. A. Ability of iron to promote surfactant peroxide decomposition and oxidize alpha-tocopherol. *J. Agric. Food Chem.* **1999**, *47*, 4146−4149.

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