Effects of emulsifier charges on the oxidative stability in oil-in-water emulsions under riboflavin photosensitization

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Received March 15, 2016 Revised June 15, 2016 Accepted June 15, 2016 Published online August 31, 2016

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pISSN 1226-7708 eISSN 2092-6456

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Abstract The oxidative stability in oil-in-water (O/W) emulsions containing different emulsifier charges was tested under riboflavin photosensitization by analysis of headspace oxygen content and lipid hydroperoxides. Sodium dodecyl sulfate (SDS), Tween 20, and cetyltrimethylammonium bromide (CTAB) were selected as anionic, neutral, and cationic emulsifiers, respectively. The O/W emulsions containing CTAB had lower oxidative stability than those with SDS and Tween 20. The addition of ethylenediaminetetraacetic acid, a well-known metal chelator, increased the oxidative stability in O/W emulsions, irrespective of emulsifier charges. Oxidative stability in Tween 20-stabilized emulsions decreased in FeCl₃ and FeCl₂ concentration-dependent manner. However, oxidative stability in samples containing CTAB increased up to 0.5 mM of FeCl₃ and FeCl₂ and then decreased, which implies that CTAB act differently during lipid oxidation compared to SDS and Tween 20.

Keywords: emulsifier charge, riboflavin, O/W emulsion, oxidative stability

Introduction

Oxidation products from lipid-rich foods can deteriorate the nutritional values and sensory attributes in foods during production and storage. Many factors can influence the rates of lipid oxidation including degree of unsaturation in lipids, types and concentration of oxygen molecules, presence of prooxidative transition metal ions and photosensitizers, types and concentration of antioxidants, and food matrix (1-5).

Oil-in-water (O/W) emulsions are composed of emulsifiersurrounding dispersed lipid particles and aqueous phase. A majority of lipid oxidation occurs at the interface between the lipid particles and aqueous phases in O/W emulsions or association colloids (1,4). Many researches have confirmed that characteristics of association colloids, the positions of antioxidants and prooxidative transition metals near association colloids, and interactions among ingredients have important effects on the rate of lipid oxidation in O/W emulsions (4,6-8).

Among the various factors for determining the oxidative stability in O/W emulsions, emulsifier charges can influence the rates of oxidation through the attraction or repulsion of transition metals (9,10). O/W emulsions containing cationic emulsifiers have been shown to demonstrate higher oxidative stability than those with anionic or neutral emulsifiers due to repulsion caused by prooxidative metal ions (7,11). However, Kancheva and Kasaikina (12) reported that cationic surfactants accelerated the lipid oxidation due to promoting the decomposition of hydroperoxides, whereas anionic SDS did not increase the rate of lipid oxidation.

Light irradiation in the presence of photosensitizers plays an important role in the oxidative stability in foods and has significant influences on the nutritional quality and flavor in foods (13). A photosensitizer can harvest light energy and transfer the energy to other chemical compounds (13). The photosensitizer can accelerate the rates of lipid oxidation (13,14). In food systems, riboflavin (RF) and chlorophylls are well-known photosensitizers (15,16). RF or chlorophyll photosensitization greatly reduces the oxidative stability in O/W emulsions through different oxidation mechanisms such as generation of singlet oxygens or superoxide anions from triplet oxygen molecules or abstraction of electrons or hydrogens from other components compared to autoxidation, which uses free radical chain reaction in unsaturated lipid moiety (13-16). Riboflavin photosensitization can accelerate the rates of lipid oxidation in different food matrix including free fatty acids (17), bulk oils (18), and milk (19). RF photosensitized oxidation can be explained by both type I and type II pathways (14,16,17,19). The type I pathway of photosensitization is to abstract electrons or hydrogen atoms from substrates generating radicals while the type II pathway of photosensitization transfers high energy to triplet oxygen forming singlet oxygen (14,20,21). Emulsion-typed food products containing RF from plants, metal chelating compounds, and emulsifying compounds with charges can be displayed under visible light irradiation in markets. However, the effects of emulsifier charges and metals on the



oxidative stability in O/W emulsions under riboflavin photosensitization have not been attempted in previous researches.

The objectives of this study were to determine the effects of emulsifier charges on the oxidative stability in O/W emulsions under RF photosensitization and to elucidate the role of iron and metal chelators in RF sensitized O/W emulsions with different charged emulsifiers.

Materials and Methods

Materials RF, sodium dodecyl sulfate (SDS), Tween 20, cetyltrimethylammonium bromide (CTAB), ethylenediaminetetraacetic acid (EDTA), FeCl₂, and FeCl₃ were purchased from Sigma-Aldrich (St. Louis, MO, USA). Corn oil was purchased from a local grocery market (Suwon, Korea). Other reagent-grade chemicals were obtained from Daejung Chemical Co. (Seoul, Korea).

Sample preparation for the emulsion and photosensitized oxidation

O/W emulsions were prepared according to a method previously described by Yi *et al.* (22). Briefly, aqueous phase was prepared by adding anionic, neutral, and cationic emulsifiers to pH 6.70 deionized water at a concentration of 0.25% (w/w), and then the aqueous phase was combined into 2.5% (w/w) corn oil. A coarse emulsion was made by homogenizing the mixture for 3 min using an HB501 (Tefal, Rumilly, Haute-Savoie, France) and then was passed three times through a two-valve high-pressure homogenizer (Taewon Chemical, Suwon, Korea) at 4,000 psi. After O/W emulsions were prepared, RF was added to the emulsions for a final molarity of 0.13 mM. The pH of emulsion with anionic, neutral, and cationic emulsifiers were 6.80, 6.03, and 6.53, respectively (data not shown).

Two milliliters of each emulsion were sealed air-tight 10 mL vials (Samwoo, Seoul, Korea) with rubber septa (Samwoo) and aluminum caps (Samwoo). Sample vials were stored under visible light irradiation at 1,333 lux light intensity for 48 h and sampled at 0, 12, 24, and 48 h. In addition, samples not treated with RF were also prepared, which were samples for photooxidation. Sample bottles were prepared in triplicate at each sampling point.

To study the metal chelating effect, EDTA was added to O/W emulsions containing RF and anionic, neutral, and cationic emulsifiers. After preparation of O/W emulsions containing RF, EDTA was added at a concentration of 10 mM and then serially diluted to final molarities of 0.1, 0.5, 1.0, 5.0, and 10 mM EDTA. Samples were treated under fluorescent light for 24 h. Samples were prepared in triplicate.

The effects of transition metals, such as $FeCl_3$ and $FeCl_2$, were determined in O/W emulsions with neutral and cationic emulsifiers. O/W emulsions containing anionic emulsifiers were not stable at the tested concentration of transition metal. After preparation of emulsions containing RF, $FeCl_3$ or $FeCl_2$ was added to the emulsion at a concentration of 10 mM and then samples were serially diluted to

final molarities of 0.1, 0.5, 1.0, 5.0, and 10 mM \mbox{FeCl}_3 or $\mbox{FeCl}_2.$ Samples were treated under fluorescent light for 12 h. Samples were prepared in triplicate.

Zeta-potential and size analysis O/W emulsions were analyzed for zeta-potential and droplet size using a zeta-potential and size analyzer (Nanotrac Wave, Microtrac, PA, USA). The instrument determines droplet sizes in O/W emulsion based on dynamic light scattering phenomenon.

Headspace oxygen analysis The headspace oxygen in air-tight sample bottles was analyzed according to a method of Kim *et al.* (23) to determine the degree of oxidation. Headspace gas of 30μ L was transferred from each sample bottle using an air-tight syringe to a GC- thermal conductivity detector (TCD). A Hewlett-Packard 7890 GC (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a 60/80 packed column (3.0 m x 2 mm ID, Restek Ltd., Bellefonte, PA, USA) and a TCD from Agilent Technologies was used. The flow rate of helium gas was 20 mL/min. Temperatures of the oven, injector, and a TCD were 60, 180, and 180°C, respectively.

Analysis of lipid hydroperoxides Lipid hydroperoxides were analyzed using a method previously described by Yi *et al.* (21). The sample of 0.2 mL was mixed with 1.5 mL isooctane/2-propanol (3:2, v:v), vortex-mixed three times for 10 s, and centrifuged for 3 min at 2,000x *g*. The upper layer of 0.2 mL was collected and mixed with 2.8 mL of methanol/1-butanol (2:1, v:v). 30 µL of thiocyanate/Fe²⁺ solution was added to the mixture and vortex-mixed for 10 s. The thiocyanate/Fe²⁺ solution was made by mixing equal volumes of 3.94 M thiocyanate solution with 0.072 M Fe²⁺ solution (obtained from the supernatant of a mixture of one part of 0.144 M FeSO₄ and one part of 0.132 M BaCl₂ in 0.4 M HCl). The samples were stood for 20 min at room temperature and absorbance at 510 nm was measured using a UV/VIS-spectrometer (Genesis 10 UV, Thermo Fisher Scientific, Waltham, MA, USA). The concentration of lipid hydroperoxide was calculated using a cumene hydroperoxide standard curve.

Statistical analysis Data on the headspace oxygen content and lipid hydroperoxides were analyzed statistically by analysis of variance (ANOVA) and the least square difference method using the SPSS software program (SPSS Inc., Chicago, IL, USA). A p value <0.05 was considered significant.

Results and Discussion

Effects of emulsifier charges on the droplet size and zeta-potential in O/W emulsions Zeta-potential and the size of dispersed droplets in O/W emulsions containing anionic, neutral, and cationic emulsifiers are shown in Table 1. Zeta-potential in O/W emulsions containing RF with anionic, neutral, and cationic emulsifiers was –

 Table 1. Effects of emulsifier charges on the droplet size and zeta-potential in O/W emulsions

		Droplet size (nm)	Zeta-potential (mV)	
w/ RF ¹⁾	SDS ¹⁾	111.97±11.05 ²⁾	-47.00±0.95 ²⁾	
	Tween 20	159.97±15.26	-32.23±2.11	
	CTAB	141.80±12.30	36.03±0.58	
w/o RF	SDS	119.40±13.22	-49.00±1.18	
	Tween 20	147.03±5.16	-31.70±1.51	
	CTAB	155.83±12.32	35.90±0.85	

¹⁾w/RF' and 'w/o RF' are O/W emulsions with or without riboflavin, respectively. SDS and CTAB are sodium dodecyl sulfate and cetyltrimethylammonium bromide, respectively.

²⁾mean±standard deviation (*n*=3).

47.0, -32.2, and 36.0 mV, respectively, whereas those in samples without RF was -49.0, -31.7, and 35.9 mV, respectively (Table 1). As expected, the cationic emulsifiers produced positively-charged surfaces, while anionic and neutral emulsifiers resulted in negatively charged surfaces. The mean size distribution of dispersed droplets in O/W emulsions containing RF with anionic, neutral, and cationic emulsifiers was 120.0, 160.0, and 141.8 nm, respectively whereas those in samples without RF was 119.4, 147.0, and 155.8 nm, respectively (Table 1). Therefore, the addition of RF did not change

the droplet size or zeta-potential in O/W emulsions irrespective of emulsifier charges.

Generally, zeta-potential around ±30 mV means formation of stable O/W emulsion. High zeta-potential implies that the surface of dispersed droplets is sufficiently surrounded with emulsifiers (24). The O/W emulsions were stable under our experimental conditions.

Effects of emulsifier charges on the oxidative stability in O/W emulsions under riboflavin photosensitization The effects of anionic, neutral, and cationic emulsifiers on the headspace oxygen content in O/W emulsions with or without RF under light and dark condition are shown in Fig. 1. The O/W emulsions containing RF under light after 48 h had significantly less headspace oxygen after 48 h under light than those before light irradiation, irrespective of emulsifier charges (p<0.05) (Fig. 1A), which implies that RF photosensitization accelerated the consumption of headspace oxygen. However, headspace oxygen content among samples were not significantly different during the oxidation study, irrespective of emulsifier charges (p>0.05) (Fig. 1A). Therefore, all of the emulsions had similar degrees of oxygen consumption after 48 h.

Headspace oxygen content in CTAB-stabilized O/W emulsions was significantly lower than that in SDS- or Tween 20-stabilized emulsions



Fig. 1. Effects of cationic, neutral, and anionic emulsifiers on the headspace oxygen content in oil-in-water emulsions with riboflavin under light (A), without riboflavin under light (B), with riboflavin in the dark (C), and without riboflavin in the dark (D) for 48 h. Different letters are significantly different at 0.05 at the same treatment time.

without RF under light (p<0.05), with RF in the dark, and without RF in the dark. Emulsions with SDS had significantly less headspace oxygen content than those with Tween 20 (p<0.05) (Fig. 1B). This indicates that, the cationic emulsifier (CTAB) accelerated lipid oxidation, indicated by the consumption of headspace oxygen in O/W emulsions (Fig. 1B, 1C, and 1D) followed by the anionic emulsifier (SDS) and the neutral emulsifier (Tween 20) under autoxidation (Fig. 1B).

The effects of anionic, neutral, and cationic emulsifiers on the lipid hydroperoxides in O/W emulsions with or without RF under light and dark conditions are shown in Fig. 2. Lipid hydroperoxides in Tween 20-stabilized emulsions had the highest levels followed by those in SDS- and CTAB-stabilized emulsions with RF under light (Fig. 2A). CTAB-stabilized emulsions without RF under light (Fig. 2B) with RF in the dark (Fig. 2C), and without RF in the dark (Fig. 2D) had significantly higher levels of lipid hydroperoxides than SDS- or Tween 20-stabilized emulsions (p<0.05) during 48 h.

The O/W emulsions without RF under light and dark conditions consistently showed that the rate of lipid oxidation was most effectively accelerated by the cationic emulsifiers, followed by anionic emulsifiers and neutral emulsifiers, based on the results of headspace oxygen analysis in Fig. 1 and the lipid hydroperoxide assay in Fig. 2. However, RF photosensitization showed a discrepancy between headspace oxygen and lipid hydroperoxide assays, which could be due to the sensitivity of assays (Fig. 1A and 2A) for determination of lipid hydroperoxides and headspace oxygen or the difference in emulsifier effects on the consumption of headspace oxygen and the formation of lipid hydroperoxides.

The oxidative stability of O/W emulsion depends on the surface charges of the lipid droplets at which lipid oxidation takes places (11,25,26). Mei et al. (11) reported that O/W emulsions made of SDS were associated with cationic ferric (Fe³⁺) and ferrous (Fe²⁺) ions, whereas those made of dodecyltrimethylammonium bromide (DTAB, cationic) and polyoxyethylene 10 lauryl ether (Brij, nonionic) were not. In cases of SDS-stabilized O/W emulsions, increasing of Fe²⁺ concentrations changed the zeta-potentials and increased the rate of lipid oxidation. However, different results have been reported in response to other experimental conditions. Kancheva and Kasaikina (12) reviewed that cationic surfactants in triacylglycerols promoted the decomposition of hydroperoxides into free radicals resulting in an increase in lipid oxidation, whereas anionic SDS did not increase the rate of lipid oxidation. These contradicting reports on the effects of emulsifier charges on the oxidative stability in lipids have been noted by Sun et al. (10).



Fig. 2. Effects of cationic, neutral, and anionic emulsifiers on the lipid hydroperoxides in O/W emulsions with riboflavin under light (A), without riboflavin under light (B), with riboflavin in the dark (C), and without riboflavin in the dark (D) for 48 h. Different letters are significantly different at 0.05 at the same treatment time.

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	Headspace oxygen content (%)			Lipid hydroperoxides (mmol/kg oil)		
	SDS	Tween 20	CTAB	SDS	Tween 20	СТАВ
0 mM	17.59±0.04 ¹⁾ c ²⁾	18.41±0.06bc	16.83±0.16a	74.95±5.41a	46.99±1.83ab	144.83±15.43a
0.1 mM	18.39±0.43b	18.04±0.14d	16.40±0.31d	81.52±10.75a	53.02±6.27a	155.12±9.39a
0.5 mM	18.55±0.46b	18.35±0.22cd	16.04±0.12d	58.63±10.33b	48.42±2.17ab	124.85±4.03b
1.0 mM	19.91±0.05a	18.51±0.28bc	17.64±0.20c	13.43±2.08c	16.92±3.21b	78.58±4.47c
5.0 mM	19.92±0.04a	19.21±0.21a	19.39±0.12b	6.82±0.04c	24.75±3.21d	23.13±3.25d
10 mM	19.82±0.04a	18.73±0.19b	19.27±0.26c	7.74±0.21c	24.75±1.69c	21.71±1.66d

Table 2. Effects of addition of EDTA on the headspace oxygen content and lipid hydroperoxides in O/W emulsions containing anionic, neutral, and cationic emulsifiers after 24 h riboflavin photosensitization

¹⁾mean±standard deviation (*n*=3)

²⁾Different letters are significantly different in the same row at 0.05.

To further elucidate the possible reasons for those contradictory results related to emulsifier charges on the oxidative stability in O/W emulsions, the effects of metal chelators and transition metals were tested.

Effects of metal chelators on the oxidative stability in O/W emulsions with cationic, neutral, and anionic emulsifiers The effects of EDTA on the headspace oxygen content and lipid hydroperoxide values in O/W emulsions containing anionic, neutral, and cationic emulsifiers after 24 h RF photosensitization are shown in Table 2. As the concentration of EDTA increased from 0 to 10 mM, the remained headspace oxygen content were higher in RF photosensitization, irrespective of emulsifier charges. The difference content of headspace oxygen content in SDS-, Tween 20-, and CTABstabilized O/W emulsions containing 0 mM and 10 mM EDTA had increased by 2.2, 0.3, and 2.4%, respectively.

In case of lipid hydroperoxides, a similar pattern was observed. Generally, the addition of EDTA significantly decreased the concentration of lipid hydroperoxides in O/W emulsions in concentration-dependent manner, irrespective of emulsifier charges compared to samples without EDTA (*p*<0.05). The concentration of lipid hydroperoxides had been significantly decreased by 67.21, 21.23, and 123.12 mmol/kg oil, respectively. Generally, emulsions containing CTAB were most sensitive to the addition of EDTA in terms of the oxidative stability followed by SDS- and Tween 20-stabilized emulsions. Therefore, the oxidative stability in CTAB-stabilized emulsions is correlated with the presence of transition metals.

Lee and Decker (16) previously reported that the oxidative stability in Tween 20-stabilized O/W emulsions under RF photosensitization increased dependence on the concentration of EDTA from 0 to 50 mM. The antioxidantive or prooxidative properties of EDTA were influenced by various factors such as the concentration and physical location of EDTA, pH in O/W emulsions, and EDTA to iron ratio (27,30).

Effects of transition metals on the oxidative stability in Tween 20and CTAB- stabilized O/W emulsions Subsequent experiments were conducted only with neutral and cationic emulsifiers-stabilized emulsions under RF photosensitization because anionic emulsifierstabilized emulsions were not stable at the tested concentration of transition metals. The effects of FeCl₃ on the headspace oxygen content (A) and lipid hydroperoxides (B) in O/W emulsions containing neutral and cationic emulsifiers for 12 h RF photosensitization are shown in Fig. 3. Headspace oxygen content decreased significantly (p<0.05) in a concentration-dependent manner in Tween 20-stabilized emulsions under RF photosensitization However, in CTAB-stabilized emulsions, adding FeCl₃ retarded the consumption of headspace oxygen up to 0.5 mM concentration and then started to increase the consumption of headspace oxygen (Fig. 3A). As the concentration of FeCl₃ increased from 0 to 10 mM, more lipid hydroperoxides formed in the O/W emulsions with a neutral emulsifiers (Fig. 3B). Lipid hydroperoxides in the O/W emulsion with CTAB decreased up to 0.5 mM FeCl₃ and then increased, which was similar to results in headspace oxygen content (Fig. 3A).

Headspace oxygen content (A) and lipid hydroperoxides (B) in O/W emulsions containing neutral and cationic emulsifiers with the addition of FeCl₂ for 12 h RF photosensitization are shown in Fig. 4. As the levels of FeCl₂ increased, the headspace oxygen content had been increased significantly (p<0.05) in Tween 20-stabilized emulsions. Headspace oxygen content in CTAB-stabilized emulsions containing 0, 0.1, 0.5, 1.0, 5.0, and 10 mM FeCl₂ after 12 h under RF photosensitization was 17.91, 18.16, 19.65, 19.73, 19.13, and 18.82 %, respectively (Fig. 4A). The addition of FeCl₂ up to a concentration of 1.0 mM increased the oxidative stability in CTAB-stabilized emulsions and then decreased with higher the concentration, which was similar to the results of FeCl₃ in Fig. 3A.

Lipid hydroperoxide values increased from 0 to 5.0 mM FeCl₂ but decreased at 10 mM FeCl₂ in the Tween 20-stabilized emulsions (Fig. 4B). Formation of lipid hydroperoxides showed lower trends at 0.1 and 0.5 mM FeCl₂ than at 0 mM FeCl₂ (p<0.05) and significantly decreased above the concentration of 1.0 mM FeCl₂ in the CTAB-stabilized emulsions (p<0.05). Therefore, transition metal acted as prooxidants in Tween 20-stabilized emulsion under RF photosensitization. However, the same transition metal performed dual roles as both an antioxidant, up to certain concentration, and then as a prooxidant at high concentrations in CTAB-stabilized emulsions under RF photosensitization.



Fig. 3. Effects of $FeCl_3$ on the headspace oxygen content (A) and lipid hydroperoxides (B) in O/W emulsions containing neutral and cationic emulsifiers after 12 h riboflavin photosensitization. Different letters are significantly different at 0.05 at the same emulsifiers.



Fig. 4. Effects of $FeCI_2$ on the headspace oxygen content (A) and lipid hydroperoxides (B) in O/W emulsions containing neutral and cationic emulsifiers after 12 h riboflavin photosensitization. Different letters are significantly different at 0.05 at the same emulsifiers.

Transition metals, including FeCl₂ and FeCl₃, are typical prooxidants in O/W emulsions (27). Ferrous ions (Fe²⁺), which are produced by FeCl₂, are involved in the decomposition of lipid hydroperoxides (LOOH) into hydroxyl radicals (•OH) or alkoxy radicals (LO•) through the Fenton reaction (28). Ferric ions (Fe³⁺) are involved in the decomposition of α -tocopherols (9) and are readily reduced into ferrous ions (Fe²⁺) by the activity of reducing agents. However, the antioxidant properties of ferric or ferrous ions have never before been reported in the literature.

The current results on O/W emulsions with cationic emulsifiers and non-buffer system did not agree with the previous report of Mei *et al.* (11), which used buffer solution in aqueous phase. Metal ions can initiate lipid oxidation by abstracting electrons from unsaturated fatty acids and through the decomposition of lipid hydroperoxides (29). CTAB, a cationic emulsifier, might be involved in the initiation step of lipid oxidation through electron attraction, which accelerated the rates of lipid oxidation (Fig. 1). CTAB might also hinder the activity of transition metals due to the same cationic properties. The addition of excessive transition metals, including FeCl₂ and FeCl₃, enhanced the oxidative stability in CTAB-stabilized O/W emulsions up to a certain concentration, based on data presented in Fig. 3 and 4. The antioxidant properties of transition metals might be due to the repulsive forces between the same positively-charged CTAB and transition metals on the oil-water interfaces. Up to a certain concentration (0.5 mM FeCl₃), both CTAB and transition metals might not be in the proper position on the interfaces of oil and water and the rates of lipid oxidation then decrease.

The prooxidative results of high concentrations of transition metals shown in Fig. 3 and 4 could be due to the competition on the electrons in unsaturated fatty acids between CTAB and transition metals, thereby increasing the decomposition rates of LOOH by transition metals. The presence of a high concentration of EDTA greatly reduced the prooxidative activity of CTAB, which implies that the prooxidative properties of CTAB are closely related to the activity of transition metals (Table 2). Prooxidant properties of EDTA were reported when ratio of concentration of EDTA and iron was 1 or less (30).

This prooxidative effect of a cationic emulsifier might be caused by bromide ions. Kanner and Kinsella (31) tested the rates of lipid peroxidation by bromide ions in a lactoperoxidase/ H_2O_2 /halide system and found that the bromide ions could accelerate the rates of oxidation.

In conclusion, the cationic emulsifier-stabilized O/W emulsions had lower oxidative stability followed by samples with anionic and then neutral emulsifiers under photooxidation or autoxidation. The addition of the metal chelator significantly increased the oxidative stability, whereas transition metals showed prooxidative and antioxidative properties depending on its concentration in CTABstabilized O/W emulsions under RF photosensitization. Prooxidative properties of CTAB in O/W emulsions could be due to the acceleration of hydroperoxides by CTAB and/or the prooxidative properties of bromide ions, which need further researches.

Acknowledgment This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2013R1A2A2A01067293) and (No. 2014R1A2A1A1105 0047).

Disclosure The authors declare no conflict of interest.

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