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Effect of Glutamic Acid and Monosodium Glutamate on Oxidative Stability of Riboflavin Photosensitized Oil-in-Water Emulsion

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Abstract

Effects of glutamic acid (Glu) and monosodium glutamate (MSG) on oxidative stability of oil-in-water (O/W) emulsions with different emulsifier charges during riboflavin (RF) photosensitization were evaluated by analyzing headspace oxygen content and conjugated dienes. Cetyltrimethylammonium bromide (CTAB), Tween 20, and sodium dodecyl sulfate (SDS) were used as cationic, neutral, and anionic emulsifiers, respectively. Glu acted as an antioxidant in CTAB- and Tween-20-stabilized O/W emulsions during RF sensitization, whereas Glu acted as prooxidants in SDS-stabilized O/W emulsions in the dark. However, adding MSG did not have a constant impact on the degree of oxidation in O/W emulsions irrespective of the emulsifier charge. In RF-photosensitized O/W emulsions, the emulsifier charge had a greater influence on antioxidant properties of Glu than on those of MSG.

Key words: glutamic acid, monosodium glutamate, emulsifier charge, O/W emulsion, oxidative stability, riboflavin photosensitization

Introduction

Some amino acids and their derivatives can add taste to foods. Tyrosine, methionine, and histidine have a sweet taste, tryptophan and glycine have a bitter taste (Schiffman & Dackis 1975), and glutamic acid (Glu) and aspartic acid have a sour taste (Zhang et al. 2013). Monosodium glutamate (MSG) is a sodium salt of Glu and is a major taste compound that provides the 'umami' flavor to foods (Caliroli et al. 2008), which is an important sensory attribute that influences consumer acceptance of foods. The annual production of MSG was approximately 2 million tons in the year 2007 (Sano C 2009), and the demand for MSG is on the rise, especially in Asian countries, including China, Indonesia, Vietnam, Thailand, and Taiwan. Because food industries use substantial amounts of MSG and amino acids for providing desirable flavor to processed foods, it is necessary to understand the physicochemical properties of MSG and Glu in food systems.

The oil-in-water (O/W) emulsion is an important physical matrix in foods that are composed of dispersed lipid particles surrounded by emulsifiers and aqueous continuous phase. Oxidative stability is one of the key factors, which determines the sensory attributes in O/W emulsion-type foods. The rates of lipid oxidation in O/W emulsions are influenced by many factors, including the degree of unsaturation in dispersed lipids, emulsifier charges, types and concentration of oxygen molecules, and the presence of antioxidants and prooxidants (McClements & Decker 2000; Chaiyasit et al. 2005; Yi et al. 2016). In addition, prooxidative metal ions and interfacial characteristics of lipid droplets greatly influence the rates of lipid oxidation in O/W emulsions (Mei et al. 1998a; Mei et al. 1998b; Chaiyasit et al. 2005; Laguerre et al. 2015). Therefore, in the industry, measures such as vacuum packaging, low-temperature storage, encapsulation of sensitive additives, and the addition of antioxidants are implemented to prevent lipid oxidation (Berton-Carabin et al. 2014). When foods containing photosensitizers are exposed to light, chemical reactions occur due to photosensitization, which affects the oxidative stability and quality

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of foods. Riboflavin (RF) is a representative hydrophilic photosensitizer (Evans et al. 2002). Lee & Decker (2011) reported that RF photosensitization could induce significant changes in the rates of lipid oxidation in O/W emulsions.

Some amino acids possess antioxidant properties. Based on 2,2-diphenyl-1-picrylhydrazyl, 2,2'-azino-bis(3-ethylbenz-thiazoline-6-sulfonic acid) and ferric reducing antioxidant powder assays, researchers have reported that cysteine has significantly high antioxidant activity compared to that of other amino acids (Pérez-Jiménes & Saura-Calixto 2006; Ka et al. 2016). The antioxidant properties of Glu or aspartic acid are significantly low compared to those of cysteine *in vitro* (Ka et al. 2016). However, the antioxidant properties of Glu have been reported in spermatozoa, where it is involved in protecting the plasma membrane from damage by lipid peroxides (Susetyarini RE 2015). Although Glu and MSG are important ingredients in foods, studies regarding their effects on the oxidative stability of O/W emulsions during RF photosensitization are rare in the literature.

The objective of this study was to determine the effects of Glu and MSG on the oxidative stability of O/W emulsions with different emulsifier charges and Glu and MSG concentrations during RF photosensitization.

Materials and Methods

1. Materials

Glu, MSG, RF, cetyltrimethylammonium bromide (CTAB), Tween 20, and sodium dodecyl sulfate (SDS) 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).

2. Sample Preparation for the Emulsion and Photosensitization

The O/W emulsions were prepared according to the method reported by Yi et al. (2016). The cationic, neutral, and anionic emulsifiers were CTAB, Tween 20, and SDS, respectively. The emulsifiers were independently added to deionized water at a concentration of 0.25% (w/w), and then varying concentrations of Glu or MSG were added [100, 1,000, and 10,000 ppm (w/w)]. Corn oil was mixed with the above solution at a concentration of 2.5% (w/w). A coarse emulsion was prepared by homogenizing the above mixture for 3 min using an HB501 (Tefal, Haute-Savoie, France) and passed three times through a nano disperser (ISA-NLM100, Ilshin Autoclave Co., Ltd., Daejoen, Korea) at 34.47 MPa. RF was added to the emulsions to achieve a concentration of 0.13 mM. Sample bottles containing 2 mL emulsion were stored under light (1,333 lux) for 60 h and samples were collected every 20 h. One set of bottles were wrapped with aluminum foil so that the bottles were in the dark. Samples to which Glu or MSG were not added were regarded as controls. Samples were prepared in triplicate at each sampling point (Fig. 1).

3. Zeta Potential and Droplet Size Analysis

The Zeta potential was analyzed based on the method reported by Kim et al. (2016). Zeta potential indicates the difference in potential between the surface of the tightly bound layer of ions on the particle surface and the region of the solution. In general, zeta potential determines emulsion stability. Emulsions containing high zeta potential values above 25 mV are considered more stable. Particle size has a direct impact on the physical stability of the emulsion (the smaller the dispersed particles, the more stable the system). The zeta potential and droplet size of O/W emulsions were determined using a zeta potential analyzer (Nanotrac Wave; Microtrac Inc., Montgomeryville, PA, USA) before and after RF photosensitization.

4. Headspace Oxygen Analysis

Lipid oxidation occurs as lipids react with oxygen, and the headspace oxygen content was analyzed to confirm the reduction

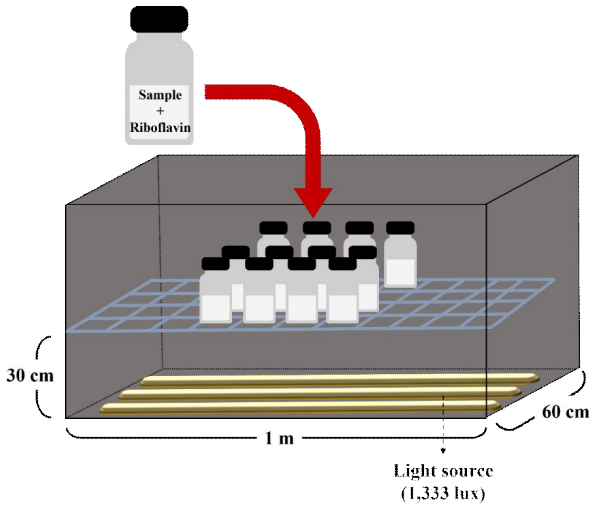

Fig. 1. Schematic design of the photooxidation device.

oxygen levels during lipid oxidation. The headspace oxygen content was analyzed based on the method reported by Yi et al. (2016). Thirty microliters of headspace gas were removed from the headspace in the sample bottle using an air-tight syringe and the oxygen content was determined using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). A Hewlett-Packard 7890 GC (Agilent Technologies, Inc., Santa Clara, CA, USA) was equipped with a 60/80 packed column (3.0 m×2 mm ID, Restek Ltd., Bellefonte, PA, USA) and TCD (Agilent Technologies, Inc.). The flow rate of the helium carrier gas was 200 mL/min. Temperatures of the oven, injector, and TCD were 60℃, 180℃, and 180℃, respectively.

5. Analysis of Conjugated Dienes

In the initiation step of lipid oxidation, polyunsaturated fatty acids containing two or more double bonds converted non conjugated double bonds into conjugated dienes. Conjugated dienes in the samples were determined using the method reported by Mei et al. (1998a), Lee et al. (2014) and Yi et al. (2018). The emulsion sample (120 μL) was mixed with 2.7 mL of methanol/1-butanol (2:1, v/v), and was further mixed by vortexing (three times for 10 s each). The oil phase was recovered and the absorbance at 233 nm was measured using a UV/VIS-spectrometer (Model Genesys 10uv, Thermo Fisher Scientific Inc., Waltham, MA, USA).

6. Statistical Analysis

The data for the headspace oxygen content, conjugated dienes, zeta potential, and particle sizes were analyzed statistically by ANOVA and Duncan's multiple range test using the SPSS software program version 19 (SPSS Inc., Chicago, IL, USA). A p-value < 0.05 was considered significant.

Results and Discussion

1. Effects of Glutamic Acid on the Oxidative Stability of O/W Emulsions

The effects of Glu on the headspace oxygen content (A) and conjugated dienes (B) in CTAB-stabilized O/W emulsions containing RF under light or in the dark are shown in Fig. 2. Control samples without Glu had the lowest oxidative stability, irrespective of light irradiation (Fig. 2). In case of headspace oxygen content, O/W emulsions with 10,000 ppm Glu had the highest oxidative stability among all samples, including the controls (Fig. 2A). The levels of conjugated dienes in the controls were higher than those with Glu over the course of 60

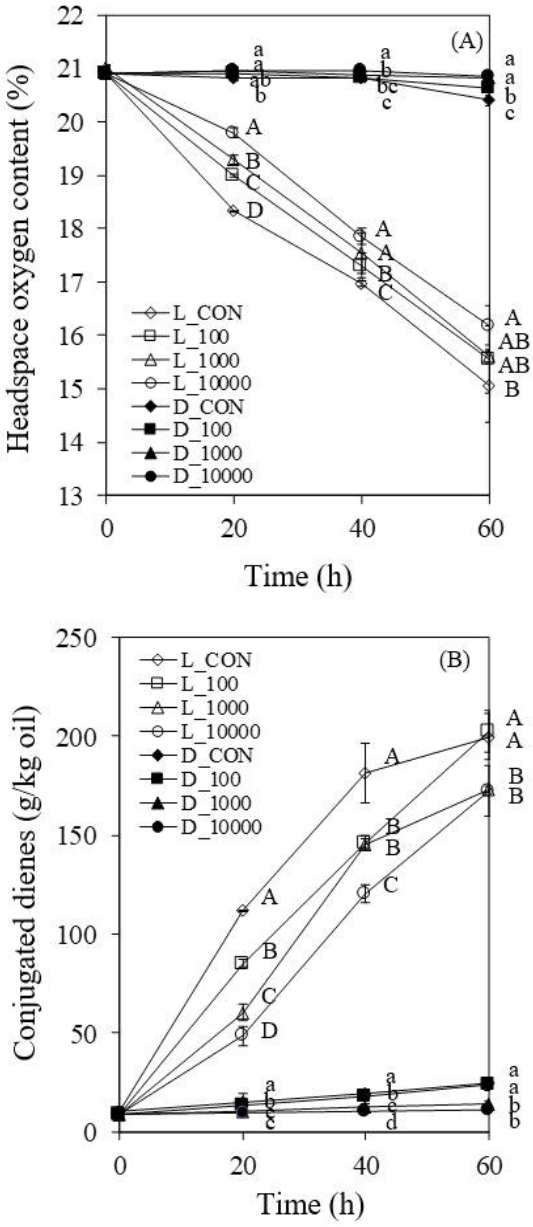

Fig. 2. Effects of glutamic acid on the changes of the headspace oxygen content (A) and conjugated dienes (B) in CTAB-stabilized O/W emulsions containing RF under light irradiation or in the dark for 60 h. 'L' and 'D' indicates the samples under light and in the dark:respectively. '100', '1,000', and '10,000' after 'L' and 'D' are 100, 1,000, and 10,000 ppm glutamic acid, respectively. Different capital and small letters are significantly different among the same treatment time under light or in the dark at 0.05, respectively.

h (Fig. 2B), which is consistent with previous results regarding headspace oxygen content (Fig. 2A). Samples with 1,000 and 10,000 ppm Glu had significantly lower levels of conjugated dienes compared to controls or samples with 100 ppm Glu (p<0.05). As for samples stored in the dark, samples with 1,000 and 10,000 ppm Glu had lower conjugated dienes values compared to controls or samples with 100 ppm Glu (Fig. 2B). Overall, Glu showed concentration-dependent antioxidant properties in CTAB-stabilized O/W emulsions, irrespective of light irradiation.

Effects of Glu on the headspace oxygen content (A) and conjugated dienes (B) in Tween 20-stabilized O/W emulsion containing RF in light and in the dark conditions are shown in Fig. 3. Samples with 10,000 ppm Glu had significantly high headspace oxygen content compared to that in other samples (p <0.05); however, samples with 0, 100, and 1,000 ppm Glu did not show any significant differences after being subjected to light for 60 h (p>0.05). In dark conditions, there were no significant differences in headspace oxygen content, irrespective of the addition of Glu (p>0.05). Samples with Glu had significantly lower levels of conjugated dienes compared to that in samples without Glu (p<0.05). Samples with 10,000 ppm Glu had significantly lower levels of conjugated dienes compared to that in controls subjected to light (p<0.05), which implies that Glu has antioxidant capacities in Tween 20-stabilized O/W emulsions during RF photosensitization.

Effects of Glu on the headspace oxygen content and conjugated dienes in anionic SDS-stabilized O/W emulsions with RF under light or in the dark are shown in Table 1. The headspace oxygen content in control samples under light and in the dark decreased from 20.9% to 14.0% and 19.2%, respectively after 60 h treatment. Under light, antioxidant or prooxidant properties of Glu were not pronounced and no significant difference was observed in headspace oxygen among samples after 60 h treatment, irrespective of the concentration of Glu (p>0.05). During RF photosensitization, Glu (10,000 ppm) showed antioxidant properties in SDS-stabilized O/W emulsions based on measured conjugated dienes. Moreover, the addition of Glu decreased the headspace oxygen content compared to that in controls kept in the dark; this result implies that the presence of Glu accelerated headspace oxygen consumption in the dark (Table 1). These findings were confirmed by the results of assays for conjugated dienes. The presence of Glu accelerated the rates of lipid oxidation in SDS-stabilized O/W emulsion (Table 1).

The concentration of Glu used in this study (100~10,000 ppm) is within the 10,000 ppm limit set by the Council of the European Union, European Parliament (1995) for foods. The content of Glu in food products from Italy and USA was between 927 to 3,410 ppm for broths, soups, and soup bases

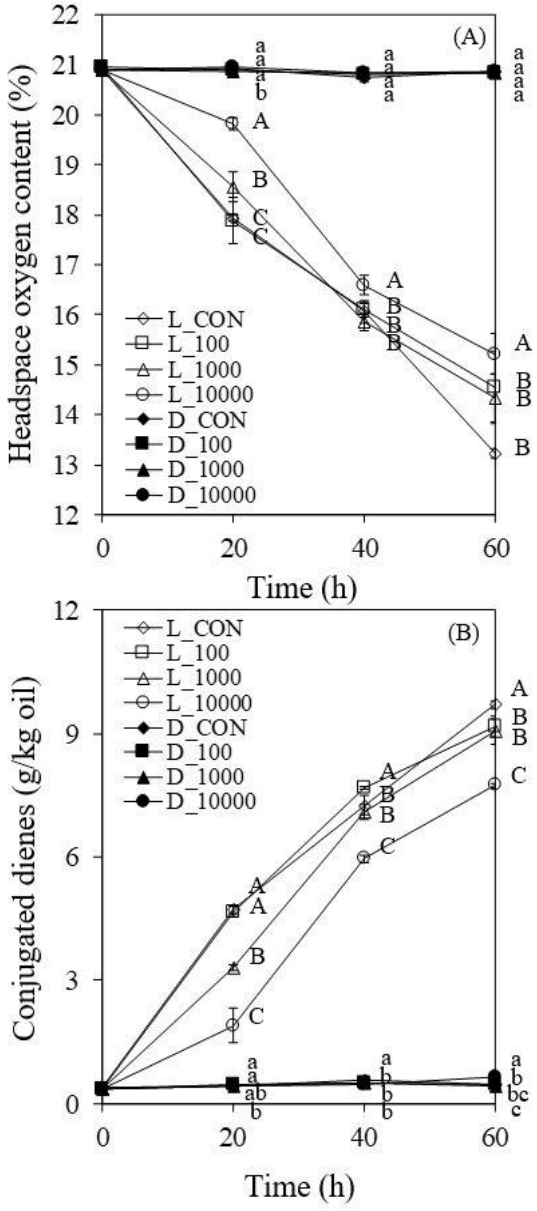

Fig. 3. Changes of the headspace oxygen content (A) and conjugated dienes (B) in Tween 20-stabilized O/W emulsions containing RF under light irradiation or in the dark for 60 h. Different capital and small letters are significantly different among the same treatment time under light or in the dark at 0.05, respectively. Abbreviations are listed in Fig. 2.

Table 1. Effect of glutamic acid on the headspace oxygen contents and conjugated dienes in SDS-stabilized oil-in-water emulsions for 60 h riboflavin photosensitization

Sample	Concentration (ppm)	Headspace oxygen content (%)				Conjugated dienes (g/kg oil)			
		0 h	20 h	40 h	60 h	0 h	20 h	40 h	60 h
Light	Control[1)]	20.9±0.1[2)]	18.7±0.1[a3)]	16.1±0.2[a]	14.0±1.3[a]	0.4±0.1	4.2±0.3[a]	7.5±0.3[a]	8.2±0.4[a]
	100	20.9±0.1	18.0±0.2[b]	15.3±0.2[b]	14.0±0.3[a]	0.9±0.1	3.9±0.2[a]	7.0±0.3[a]	8.4±0.8[a]
	1,000	20.9±0.1	18.6±0.1[a]	16.1±0.5[a]	13.9±0.5[a]	0.6±0.1	3.1±0.2[b]	6.0±0.1[b]	8.5±0.3[a]
	10,000	20.9±0.1	18.7±0.2[a]	16.5±0.5[a]	14.7±0.6[a]	0.6±0.1	2.9±0.1[b]	5.5±0.4[b]	6.8±0.4[b]
Dark	Control	20.9±0.1	20.8±0.0[a]	20.7±0.0[a]	19.2±1.4[a]	0.4±0.1	0.3±0.0[b]	1.0±0.0[d]	5.2±2.3[c]
	100	20.9±0.1	18.9±0.3[b]	16.2±0.8[c]	14.9±0.5[b]	0.9±0.1	4.3±0.6[a]	7.4±0.7[a]	9.7±0.1[a]
	1,000	20.9±0.1	19.0±0.3[b]	16.8±0.5[c]	15.9±0.5[b]	0.6±.0.1	3.7±0.9[a]	6.0±0.4[b]	7.7±0.4[ab]
	10,000	20.9±0.1	19.3±0.5[b]	17.7±0.2[b]	16.2±0.1[b]	0.6±0.1	3.2±0.9[a]	4.9±0.2[c]	7.2±0.2[bc]

1) Without amino acids.
2) Mean±standard deviation (n=3).
3) In the same column, different small letters mean significant differences (p<0.05).

with added monosodium glutamate, and was 2,660 to 7,530 ppm for salad dressings, which are mixtures of oil and water (Populin et al. 2007).

Lipid oxidation driven by RF photosensitization can undergo both type I and type II pathways (Min & Boff 2002). Compared to autoxidation at 55~60℃, RF photosensitization speeds up the rates of lipid oxidation, and more oxidizing factors are involved, including reactive oxygen species like singlet oxygen and superoxide anion, excited photosensitizers, and lipid radicals (Min & Boff 2002; Lee & Decker 2011).

It is quite interesting to note that Glu showed antioxidant properties in CTAB- and Tween 20-stabilized emulsions under light, while its prooxidative properties were displayed in SDS-stabilized O/W emulsions only in the dark. The charge of an emulsifier surrounding the dispersed lipid particles can affect the oxidative stability by attracting or repelling metal (Mei et al. 1998a; Sun et al. 2011). O/W emulsions containing a cationic emulsifier have been reported to have higher oxidative stability compared to other emulsifier-stabilized O/W emulsions, because of the repulsion between cationic transition metal ions (Mei et al. 1998b). However, the prooxidative property of CTAB was reported in O/W emulsions during RF photosensitization (Yi et al. 2016), and in fatty acid esters containing association colloids (Homma et al. 2016). Kancheva & Kasaikina (2012) reported that cationic surfactants in triacylglycerols increased the rates of lipid oxidation by breaking-down hydroperoxides into free radicals. In addition, the higher pH of the CTAB solution might be the underlying cause of the prooxidant properties of CTAB in O/W emulsions (Yi et al. 2018). Glu in anionic-charged O/W emulsions may attract more transition metals like iron and copper, and the rates of lipid oxidation accelerate in SDS-stabilized O/W emulsions in the dark.

2. Effect of Addition of Monosodium Glutamate on the Oxidative Stability of O/W Emulsions

Effects of MSG on the headspace oxygen content and conjugated dienes in O/W emulsions during light irradiation or in the dark are shown in Table 2. All samples had lower headspace content compared to that in the 0 h sample during RF photosensitization, irrespective of emulsifier charge. CTAB-stabilized O/W emulsion had the highest headspace oxygen content followed by SDS-stabilized and Tween-20-stabilized O/W emulsions (in decreasing order) after 60 h RF photosensitization (Table 2). The consumption of headspace oxygen increased significantly when MSG was added to the O/W emulsion stabilized with CTAB (p<0.05), implying that MSG acted as a prooxidant. There were no significant differences in the headspace oxygen content between Tween-20- and SDS-stabilized samples during RF photosensitization for 60 h (p>0.05), implying that the added MSG did not alter the rates of lipid oxidation.

In the dark, MSG showed antioxidant properties in CTAB-stabilized and SDS-stabilized emulsions based on the headspace oxygen and conjugated diene content. However, the prooxidant properties of MSG were found in Tween-20-stabilized samples (Table 2). The addition of MSG provides

Table 2. Effect of monosodium glutamate on the headspace oxygen contents and conjugated dienes in oil-in-water emulsions for 60 h riboflavin photosensitization with different emulsifier charges

Sample		Concentration (ppm)	Headspace oxygen content (%)			Conjugated dienes (g/kg oil)		
			0 h	40 h	60 h	0 h	40 h	60 h
Light	CTAB	Control[1)]	21.0±0.0[2)]	17.2±0.2[a3)]	16.4±0.3[a]	0.5±0.0	8.5±0.2[a]	9.8±0.6[a]
		100	20.9±0.0	16.6±0.1[bc]	15.6±0.2[b]	0.4±0.0	8.2±0.3[a]	9.6±0.4[a]
		1,000	21.1±0.0	16.3±0.3[c]	15.7±0.5[b]	0.4±0.0	8.1±0.3[ab]	9.3±0.3[ab]
		10,000	21.0±0.0	16.8±0.1[b]	15.2±0.3[b]	0.4±0.0	7.6±0.4[b]	8.7±0.0[b]
	Tween 20	Control	20.9±0.0	16.1±0.2[a]	13.2±0.1[a]	0.4±0.0	7.2±0.2[ab]	9.7±0.1[c]
		100	20.9±0.0	15.2±0.1[b]	13.2±0.4[a]	0.3±0.0	7.9±0.4[a]	12.4±0.5[a]
		1,000	20.9±0.0	15.1±0.2[b]	13.3±0.1[a]	0.3±0.0	8.0±0.2[a]	12.6±0.2[a]
		10,000	20.9±0.0	15.7±0.3[a]	13.7±0.4[a]	0.4±0.0	6.7±0.5[b]	10.5±0.2[b]
	SDS	Control	20.9±0.0	16.1±0.2[a]	14.0±1.3[a]	0.4±0.0	7.5±0.3[a]	8.2±0.4[b]
		100	20.9±0.0	16.2±0.3[a]	14.5±0.2[a]	0.4±0.0	7.6±0.2[a]	9.0±0.2[a]
		1,000	20.9±0.0	16.3±0.2[a]	14.7±0.2[a]	0.4±0.0	7.5±0.3[a]	9.0±0.5[a]
		10,000	21.0±0.0	16.4±0.2[a]	14.8±0.2[a]	0.4±0.0	7.5±0.9[a]	8.3±0.2[b]
Dark	CTAB	Control	21.0±0.0	20.8±0.0[a]	20.4±0.1[b]	0.5±0.0	1.0±0.0[a]	1.2±0.2[a]
		100	20.9±0.0	20.8±0.1[a]	20.8±0.1[a]	0.4±0.0	0.8±0.1[ab]	0.8±0.2[b]
		1,000	21.1±0.0	20.8±0.0[a]	20.8±0.1[a]	0.4±0.0	0.7±0.1[bc]	0.8±0.0[b]
		10,000	21.0±0.0	20.9±0.0[a]	20.8±0.0[a]	0.4±0.0	0.6±0.0[c]	0.6±0.1[c]
	Tween 20	Control	20.9±0.0	20.9±0.0[a]	20.7±0.1[a]	0.4±0.0	0.6±0.0[b]	0.5±0.0[b]
		100	20.9±0.0	20.6±0.1[b]	20.6±0.0[b]	0.3±0.0	0.7±0.1[ab]	0.7±0.1[a]
		1,000	20.9±0.0	20.5±0.1[b]	20.4±0.2[b]	0.3±0.0	1.0±0.3[a]	0.7±0.1[a]
		10,000	20.9±0.0	20.4±0.1[c]	20.3±0.0[b]	0.4±0.0	0.7±0.0[ab]	0.8±0.0[a]
	SDS	Control	20.9±0.0	20.7±0.0[ab]	19.2±1.4[a]	0.4±0.0	1.0±0.0[ab]	5.2±2.3[a]
		100	20.9±0.0	20.6±0.0[b]	19.2±0.8[a]	0.4±0.0	1.3±0.5[a]	3.2±0.5[ab]
		1,000	20.9±0.0	20.7±0.1[ab]	19.6±0.9[a]	0.4±0.0	0.9±0.1[ab]	2.6±1.2[b]
		10,000	21.0±0.0	20.8±0.1[a]	20.7±0.0[a]	0.4±0.0	0.6±0.0[b]	0.7±0.0[b]

[1)] Without amino acids.
[2)] Mean±standard deviation (n=3).
[3)] In the same column, different small letters mean significant differences (p<0.05).

antioxidant properties at 10,000 ppm in O/W emulsions with anionic and cationic emulsifiers in the dark. Compared to the results obtained with Glu, the antioxidant or prooxidant activities of MSG were not substantial.

3. Zeta Potential and Droplet Size Analysis of O/W Emulsions Containing Glu or MSG

Changes in zeta potential and droplet size in O/W emulsions with or without Glu and MSG with different emulsifier charges are shown in Table 3. As the added Glu increased from 0 to 10,000 ppm, the zeta potential of CTAB-stabilized O/W emulsions increased from 47.1 to 81.5 mV, and this trend was observed even after the 60 h RF photosensitization period. The added Glu may help in the aggregation of more CTAB at the interface of the oil-water droplets. Whereas the zeta potential in Tween 20-stabilized O/W emulsions did not show consistent changes with respect to the presence of Glu. The zeta potential of SDS-stabilized O/W emulsions decreased from −48.8 to −66.7 mV as the concentration of Glu increased from 0 to 10,000 ppm and remained at this level after 60 h treatment (Table 3). Similar to the results of CTAB-stabilized samples, the presence of Glu may help locate an anionic emulsifier easily at the interface between oil-water dispersed phase.

In general, the addition of Glu induced changes in the zeta

Table 3. Changes of zeta-potential and droplet size in oil-in-water emulsions with or without glutamic acid or monosodium glutamate for 60 h with different emulsifier charges

Sample		Concentration (ppm)	Zeta-potential (mV)		Size of droplets (nm)	
			0 h	60 h	0 h	60 h
Glutamic acid	CTAB	Control[1)]	47.1±0.2[c2)3)]	67.3±7.8[b]	255.4±11.9[b]	225.7±6.0[a]
		100	71.5±0.1[b]	61.6±1.2[b]	290.2±0.1[a]	239.5±5.8[a]
		1,000	69.8±2.7[b]	70.6±2.8[b]	240.5±12.5[bc]	249.5±5.0[a]
		10,000	81.5±5.1[a]	85.7±10.2[a]	220.0±26.5[c]	217.6±38.1[a]
	Tween 20	Control	−19.8±1.1[c]	−2.8±4.0[a]	249.5±6.9[a]	248.0±19.3[a]
		100	−9.5±1.3[a]	−6.9±3.3[a]	251.3±6.4[a]	238.3±5.3[a]
		1,000	−15.2±3.2[b]	−15.3±2.5[b]	254.2±1.6[a]	253.9±2.7[a]
		10,000	−15.5±2.5[b]	−15.0±2.9[b]	256.4±5.5[a]	251.4±11.9[a]
	SDS	Control	−48.8±1.7[a]	−50.7±6.2[a]	218.6±10.4[a]	212.1±2.7[a]
		100	−55.4±1.1[a]	−56.2±1.6[ab]	218.5±4.3[a]	216.6±5.4[a]
		1,000	−53.6±0.9[a]	−59.1±2.4[bc]	216.9±3.9[a]	216.4±3.9[a]
		10,000	−66.7±7.0[b]	−65.0±0.3[c]	200.9±16.7[a]	209.3±9.8[a]
Monosodium glutamate (MSG)	CTAB	Control	47.13±0.21[b]	67.33±7.84[a]	255.37±11.91[a]	225.70±6.46[a]
		100	45.90±11.28[b]	63.03±5.83[a]	243.50±6.06[a]	224.83±20.57[a]
		1,000	56.57±4.87[b]	64.70±2.21[a]	198.57±17.76[b]	216.53±6.69[a]
		10,000	71.60±4.29[a]	60.67±7.23[a]	233.73±33.62[ab]	224.60±11.47[a]
	Tween 20	Control	−19.77±1.10[b]	−2.77±3.95[a]	249.53±6.86[a]	248.00±19.26[a]
		100	−15.33±0.23[a]	−23.97±0.57[c]	256.57±3.54[a]	250.77±5.06[a]
		1,000	−21.63±1.46[b]	−24.70±2.31[c]	252.60±15.34[a]	252.20±8.98[a]
		10,000	−21.47±1.03[b]	−19.47±1.03[b]	254.40±14.07[a]	249.57±8.36[a]
	SDS	Control	−48.80±1.71[a]	−50.67±6.16[a]	218.60±10.38[a]	212.10±2.69[a]
		100	−47.47±0.64[a]	−54.63±2.25[a]	215.10±5.07[a]	221.47±6.50[a]
		1,000	−59.03±1.32[b]	−64.63±2.19[b]	211.83±1.00[a]	218.37±6.81[a]
		10,000	−104.07±3.55[c]	−111.23±0.81[c]	214.03±5.42[a]	201.57±0.49[b]

[1)] Without amino acids.
[2)] Mean±standard deviation (n=3).
[3)] In the same column, different small letters mean significant differences (p<0.05).

potential in O/W emulsions with cationic or anionic emulsifiers. It is likely that the presence of Glu induced denser packing of emulsifiers at the oil-water interface. The pH of the continuous phase used was 5.4 (Yi et al. 2018), and a negatively charged form of Glu was predominant. If Glu itself could get loaded on to the interface as an emulsifier, the zeta potential of CTAB-stabilized O/W emulsions would decrease. However, an increase in the zeta potential was observed in CTAB-stabilized O/W emulsions, indicating that Glu may not accumulate at the oil-water interface. In case of SDS-stabilized emulsions, Glu might act as an inducer of tighter packing of SDS at the oil-water interface due to the decrease in negative zeta potential.

The increased oxidative stability in CTAB-stabilized emulsions upon addition of Glu can be explained by changes in the zeta potential. Increased number of positive charges at the interface in CTAB-stabilized emulsions with added Glu might repel prooxidative transition metals, which would then retard the rates of lipid oxidation. Conversely, in SDS-stabilized emulsions with Glu, the decrease in negative charges on the droplets might attract transition metals, which would accelerate the rate of lipid oxidation (Fig. 2, Fig. 3 and Table 1).

Although the scavenging ability of free radicals or the reducing ability of ferric ions of Glu were not high enough (Pérez-Jiménes & Saura-Calixto 2006; Ka et al. 2016), Glu has

charged functional groups and are known to be antioxidants (Chen & Nawar 1991). Amino acid residues within proteins can react with singlet oxygen either via a chemical reaction or by physical quenching (Gracanin et al. 2009). However, the reactivity of Glu with singlet oxygen has not been reported in the literature. The antioxidant properties of Glu in O/W emulsions during RF photosensitization might be due to the inhibition of the type I pathway rather than the type II pathway.

The zeta potentials of CTAB-stabilized emulsions increased significantly as the concentration of MSG increased from 0 to 10,000 ppm before RF photosensitization ($p<0.05$), and those of the SDS-stabilized samples decreased significantly ($p<0.05$) (Table 3). The effects of MSG concentration on the zeta potentials of Tween 20-stabilized emulsions were not consistent. Interestingly, after 60 h of RF treatment, there was no significant variation in zeta potentials in CTAB-stabilized emulsions with different concentrations of MSG ($p>0.05$), whereas there was significant variation in SDS-stabilized emulsions with different concentrations of MSG ($p<0.05$). Anionic glutamate may get incorporated on the interface of dispersed oil droplets in SDS-stabilized emulsions and decrease the zeta potential substantially.

There were no significant differences in the droplet sizes in in samples treated for 60 h－except in case of the 10,000 ppm MSG-added SDS-stabilized emulsion－irrespective of concentration of MSG or the charge of the emulsifier ($p>0.05$), implying that the added MSG did not show emulsifying properties. Generally, the droplet sizes of CTAB- and SDS-stabilized emulsions were smaller than those of the Tween-20 stabilized samples after RF photosensitization (Table 3).

In solution, MSG gets dissociated into positive sodium ions and negative glutamate ions. The addition of sodium ions can influence the oxidative stability in O/W emulsions. Osborn-Barnes & Akoh (2003) reported that the addition of 0.5 M NaCl results in an increase in secondary oxidation in emulsions containing copper, and explained that the effects of NaCl on oxidation were caused by NaCl-induced changes in the physical properties of the emulsion droplets such as a reduction in the thickness of the double layer. Additionally, Mei et al. (1998b) reported that at NaCl concentrations greater than 17 mM, the zeta potential of the SDS emulsions became less negative. This caused a decrease in the association of iron with SDS emulsion droplets. Overall, the effects of MSG addition on oxidative stability may partly be due to the effect of the cationic sodium salt and anionic glutamate. Depending on the type of emulsifier charge, the added Glu and MSG exerted different effects on the oxidative stability.

Conclusions

The antioxidant effects of Glu and MSG on the oxidative stability were evaluated in O/W emulsions with different emulsifier charges and RF photosensitization. Glu showed antioxidant properties in emulsions containing cationic and neutral emulsifiers during RF sensitization and acted as a prooxidant in SDS-stabilized O/W emulsions in the dark. Addition of MSG did not show such prominent effects as those of Glu. The oxidative stability of foods with O/W emulsion states containing Glu or MSG should be carefully evaluated, and factors, such as the charges of on droplets, the presence of photosensitizers, and light irradiation must be taken into consideration.

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