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Volatile Release from Self-Assembly Structured Emulsions: Effect of Monoglyceride Content, Oil Content, and Oil Type

Like Mao,[†,§] Yrjö H. Roos,[§] and Song Miao*[,†]

[†]Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland

[§]School of Food and Nutritional Sciences, University College Cork, Cork, Ireland

ABSTRACT: Monoglycerides (MGs) can form self-assembled structures in emulsions, which can be used to control volatile release. In this study, initial headspace concentrations ($C_{initial}$), maximum headspace concentrations (C_{max}), release rates, and partition coefficients of propanol, diacetyl, hexanal, and limonene were determined in MG structured oil-in-water emulsions using dynamic and static headspace analyses. For all of the volatile compounds, $C_{initial}$ values above structured emulsions were significantly lower than those above unstructured emulsions and decreased with increasing MG contents ($p < 0.05$). However, volatiles had higher release rates in emulsions with higher MG contents. When oil content was reduced from 20 to 10%, $C_{initial}$ and C_{max} increased for limonene and hexanal and decreased for propanol and diacetyl. When different oils were applied, both $C_{initial}$ and C_{max} were significantly lower in medium-chain triglyceride emulsions than in soybean oil emulsions ($p < 0.05$). Static headspace analysis revealed that volatile compounds had significantly lower air−emulsion partition coefficients in the structured emulsions than in unstructured emulsions ($p < 0.05$). These results indicated that MG structured emulsions can be potentially used as delivery systems to modulate volatile release.

KEYWORDS: *emulsion, volatile release, monoglyceride, self-assembled structure, headspace, partition coefficient*

INTRODUCTION

Volatile flavor compounds are perceived when they are in contact with olfactory receptors either orthonasally by sniffing or retronasally by volatile migration during mastication. Headspace volatile concentration and speed of volatile release could largely influence flavor perception. Volatile release from emulsions is dependent on the physicochemical properties of the volatile compounds and the ingredients in the emulsions and their concentrations,[1−4] as well as emulsion properties (e.g., droplet size, viscosity).[4−6] Of these factors in oil-in-water (O/W) emulsions, oil plays a dominant role on volatile release. Oils can act as volatile precursors, as solvents for volatiles, and as volatile release modulators.[7] Variation in oil content or oil nature may lead to significantly different volatile release profiles. It has been well documented that reduction in oil content can promote the release of lipophilic volatile compounds, and headspace concentration of volatiles above an emulsion with lower oil content was normally higher.[1,8−10] Fat-free products therefore often show an undesirable transient volatile burst, as the release is not mediated by a fat phase.[11] Only a small portion of the volatile flavors are hydrophilic, and they behave differently. Several studies showed that the release of hydrophilic volatile compounds was not, or even positively, affected by increasing oil contents.[9,11,12] On the other hand, different types of oils varying in fatty acid composition (e.g., chain length, saturation level, chain arrangement) and physical state (solid/liquid fat ratio) had different affinities for volatile compounds, giving different effects on volatile release.[11,13,14] Moreover, oil can influence volatile release indirectly by changing emulsion properties.[4] In some systems, the impact of oil was so dominant that binding effects of other food ingredients (e.g., proteins) to volatile compounds were insignificant.[13,15]

Monoglycerides (MGs) are common food emulsifiers, and they can be used to modify oil properties.[16,17] When MG is dispersed in oil above the melting point, it forms self-assembled structures (liquid crystals) on cooling.[18] Such crystalline structures can be used as delivery systems, to protect sensitive bioactive substances, to solubilize drugs, and to control the release of active compounds.[16,19] Furthermore, in an oil−water dispersion MG could develop into a highly hydrated crystalline lamellar phase (Lα) and form a mesomorphic gel with some solid fat-like characteristics, which could be used in fat-reduced food.[20,21] The use of MG self-assembled structures to control volatile release from emulsions has only been reported recently. In MG structured W/O microemulsions, Vauthey et al.[22] found increased volatile release of both lipophilic and hydrophilic compounds, whereas Landy et al.[23] reported that lipophilic volatile compounds were retained at a higher level in MG structured emulsions, in comparison with unstructured W/O emulsions. In MG structured oil-in-water gel systems, Calligaris et al.[21] discovered that the equilibrium concentration of limonene in the headspace of MG gel was significantly lower than that of a conventional emulsion. Phan et al.[24] made MG structured O/W emulsions with low oil content, in which delayed volatile release was also observed. Therefore, emulsions containing MG self-assembled structures have some potential to act as delivery systems for volatile compounds. However, further studies are required to better understand the influence of MG self-assembled structures on volatile release from emulsion systems.

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Table 1. Formulation Map of the Emulsions Tested and Properties of the Emulsions[a] (Mean ± SD, $n \geq 3$)

oil type[b]	oil content (%)	MG[c] content (%)	size (nm)	PdI[d]	viscosity[e] (mPa.S)
SO	20	0	283.7 ± 2.6a	0.26 ± 0.01	3.40 ± 0.16a
SO	20	0.5	277.3 ± 1.9b	0.24 ± 0.02	14.05 ± 0.68b
SO	20	1	254.7 ± 1.8c	0.22 ± 0.01	16.52 ± 0.90c
SO	20	2	205.4 ± 2.4d	0.16 ± 0.01	58.52 ± 2.13d
SO	10	0	258.3 ± 2.2c	0.12 ± 0.02	3.30 ± 0.12a
SO	10	2	192.2 ± 2.3e	0.18 ± 0.01	36.40 ± 0.85e
MCT	20	0	294.8 ± 3.0f	0.32 ± 0.03	3.45 ± 0.20a
MCT	20	2	183.9 ± 5.7g	0.08 ± 0.01	48.72 ± 1.52f

[a]Properties were measured after 3 days of storage (25 °C). Within a column, values with different letters are significantly different ($p < 0.05$). [b]SO, soybean oil; MCT, medium-chain triglyceride. [c]MG, monoglyceride. [d]PdI, polydispersity index. [e]Viscosities were obtained at the shear rate of 100 s^{-1} (25 °C).

The aim of the present study was to investigate the effects of MG content, oil content, and oil type on the release behavior of four volatile compounds from emulsions containing MG self-assembled structure. MG formed crystalline structure in Tween 20 stabilized O/W emulsions, and volatile release modified by MG structure was measured by GC headspace analysis (dynamic and static studies). The knowledge obtained in this study might be useful in the development of novel foods with improved flavor profiles.

MATERIALS AND METHODS

Materials. Dimodan HR (Danisco, Denmark) was purchased from Cloverhill Food Ingredients Ltd. (Cork, Ireland). This product contained >90% MG (glycerol monostearate). Medium-chain triglyceride (MCT) was kindly offered by Lonza Inc. (Williamsport, PA, USA) and contained 71% caprylic acid and 29% capric acid. Polyoxyethylene sorbitan monolaurate (Tween 20), soybean oil (SO), sodium azide, and four volatile compounds, that is, 1-propanol (>99.5% purity), diacetyl (>99.5% purity), hexanal (>98% purity), and (*R*)-(+)-limonene (>97% purity), were all products of Sigma-Aldrich (St. Louis, MO, USA).

Emulsion Preparation. Tween 20 was dispersed in deionized water (1% w/w of final emulsion), and sodium azide (0.01% w/w) was added as an antimicrobial agent. For the oil phase (10 or 20% w/w), different amounts of MG were mixed with SO (or MCT), and the mixture was heated to ∼75 °C to completely dissolve MG. The aqueous and oil phases were subsequently mixed at 5000 rpm for 5 min using a Silverson high-speed blender (Silverson Machines Ltd., Chesham Bucks, UK) to form a coarse emulsion, which was further homogenized using an M110-EH Microfluidizer (Microfluidics International Corp., Newton, MA, USA) at 50 MPa for one pass. In microfluidization, a 75 μm Y-type ceramic interaction chamber was used, together with a 200 μm Z -type auxiliary processing module. The final emulsions were immediately cooled to room temperature (25 °C) with tap water and then stored in an incubator at 25 °C for future analysis.

Emulsion Characterization. Droplet sizes of the emulsions were determined by dynamic light scattering using a Zetasizer Nano-ZS90 (Malvern Instruments, Worcestershire, UK) at a fixed detector angle of 90°. Results were described as intensity mean diameter (size, nm), and polydispersity index (PdI) for size distribution.

Viscosity measurements were performed using an AR 2000ex rheometer (TA Instruments, Crawley, UK), equipped with a DIN and concentric cylinder geometry (stator inner radius = 15 mm, rotor outer radius = 14 mm, gap = 5920 μm). The test was performed over a shear rate range of 0−300 s^{-1} at 25 °C.

Differential Scanning Calorimetry. Thermal behaviors of MG in structured emulsions were analyzed using a DSC Q2000 differential scanning calorimeter (TA Instruments), on the day of sample preparation (D1), after 3 days (D4, stored at 25 °C), and after 6 days (D7, stored at 25 °C). Approximately 15−20 mg of each sample was prepared in a Tzero pan, which was sealed with a Tzero hermetic lid. An empty pan was used as a reference. The DSC sample pans were heated from 25 to 80 °C at 5 °C/min to track the melting of the crystals formed in the emulsion. The DSC was calibrated with indium at a heating rate of 5 °C/min.[25]

Flavoring of Emulsions. Stock solutions of volatile compounds were prepared by mixing four volatiles in ethanol (10% v/v for each volatile) at room temperature and equilibrated for at least 1 h. Emulsion flavoring was then performed by adding volatile solution into emulsions in gastight glass vials (20 mL, silicone/PTFE seals) (La-pha-pack GmbH, Langerwehe, Germany) to reach a concentration of 1000 mg/L for each volatile. The vials were fully filled to minimize volatile losses. Emulsions were stored at 25 °C, and headspace analysis was done on the day of emulsion flavoring (D1) or three days after (D4).

Dynamic Headspace Analysis. Headspace concentrations of the volatiles at different time points were measured using a Varian CP-3800 gas chromatograph (Varian Inc., Palo Alto, CA, USA) equipped with a ZB-5MSi capillary column (60 m, 0.25 mm i.d., film thickness = 0.25 μm) and coupled with a FID detector. Flavored emulsion (2 g) was rapidly transferred to a 20 mL headspace vial and capped immediately (silicone/PTFE seals) (La-pha-pack GmbH). The vials were incubated at 37 °C (close to temperature in oral cavity) in a Combi PAL autosampler (CTC Analytics AG, Zwingen, Switzerland). The dynamic condition was created by varying the incubation time (from 30 s to 60 min). Pre-experiment showed that sufficient headspace concentration was created after 30 s of incubation, and it was chosen as the start sampling point. Injections of the headspace (1 mL) were performed using a preheated (42 °C) 2.5 mL thermostated gastight syringe (Hamilton, Bonaduz, Switzerland) under split mode (1:10). Injector and FID temperatures were, respectively, 225 and 230 °C. The helium carrier gas velocity was 1 mL/min. The temperature program was 50 °C (4 min), raised to 200 °C at 10 °C/min rate and to 240 °C at 40 °C/min rate (2 min).[26]

Initial headspace concentration ($C_{initial}$, sampling after 30 s of incubation), maximum headspace concentration (C_{max}, the highest concentration during incubation), and release rates were adopted to describe dynamic volatile release. To quantify the concentrations of the volatiles in the headspace, calibration curves of the four volatiles were plotted using peak areas obtained from GC analysis against six known concentrations of each volatile in ethanol. The completely vaporized volatile−ethanol solution was analyzed according to the above GC methods. Results were based on triple analyses. The dynamic release of the volatiles from emulsions was expressed by plotting the headspace concentrations of each volatile (mg/L) against incubation time (min) at 37 °C. Slopes of the initial linear part of the release curves were taken as release rates (mg/L min).

Determination of Air−Emulsion Partition Coefficients. Air−emulsion partition coefficients ($K_{A/E}$) were determined by calculating the ratio of volatile concentrations in the headspace and emulsion matrix at equilibrium. Headspace concentrations were measured through static headspace analysis using the same GC method as described in dynamic headspace analysis, and samples were incubated at 37 °C for 60 min. Volatile concentration remaining in the emulsion

was then calculated by subtracting headspace volatile from the originally added volatile during emulsion flavoring.

Statistical Analysis. Statistical analysis was performed using OriginPro 7.5. All of the measurements were repeated at least three times. A one-way analysis of variance (ANOVA), followed by Tukey's test, was applied to determine significant differences between the mean values of each test. A significance level of $p < 0.05$ was used throughout the study.

RESULTS AND DISCUSSION

The emulsions had droplet sizes ranging from 183.9 to 283.7 nm, with different viscosities due to various oil compositions (Table 1) after 3 days of storage. They were stable during the testing period, and no creaming or phase separation was observed.

Formation of MG Self-Assembled Structure and Volatile Release. It was reported that in the MG structured oil-in-water gels, MG crystalline structure was formed soon after gel preparation.[20] In the present O/W emulsion systems, MG crystalline structure was developed gradually. The DSC thermogram (Figure 1) showed that only a weak melting peak

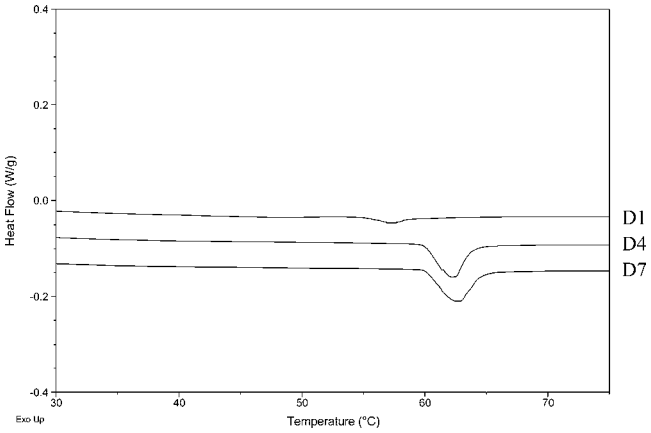

Figure 1. Melting behaviors of MG in emulsions (SO, 20% w/w; MG, 2% w/w) on day 1 (D1), day 4 (D4), and day 7 (D7) (DSC heating rate = 5 °C/min).

of MG was present in the emulsion containing 2% MG on D1, which later transferred to a big peak after 3 days of storage (D4) and remained stable during the subsequent storage (D7). Microfluidization broke oil droplets to submicrometer size and reduced concentration of impurity for nucleation, which was the main reason for the lower crystallizing rate of MG in emulsion.[27] The two peaks at different melting temperatures corresponded to the transient α form crystal and stable β form crystal.[17,25]

In the current O/W emulsions, MG crystalline structure was most likely present in the oil phase and at the interface. Yaghmure et al.[28,29] studied emulsions containing monoglyceride (with other surfactants), and reported the existence of crystalline MG in the dispersed particles using cryo-TEM (with fast Fourier transform). The result was also confirmed by small-angle X-ray scattering (SAXS) measurements. The crystalline MG in the oil droplets formed hydrophilic domains, with size smaller than 7 nm. This type of emulsion is obviously different from a water-in-oil-in-water (W/O/W) double emulsion, as the inner MG hydrophilic domains are self-assembly formed. It was also revealed that the shapes of crystalline domains in the oil droplets were neither hexosomes nor cubosomes (as normally observed in MG−water or MG−oil dispersions), but more circular. Batte et al.[20,30] reported MG crystalline structure covering oil droplets in MG−oil−water gels (O/W emulsions, with cosurfactant) through polar light microscopy, and they proposed the crystalline structure to be lamellar as XRD results indicated. They found that interfacial MG was continuous from one droplet to the next, forming a network with oil droplets being trapped. In fact, many emulsifiers possibly exist at the interface and in bulk phase. This phenomenon was widely reported in studies where a single surfactant was used to stabilize emulsions, and unabsorbed surfactant would stay in favorable phase forming micelles or reverse micelles.[17] Although MG was reported to be able to form crystalline structure in water phase,[18] it was less likely to happen in the current system because MG was first dissolved in the oil phase and MG has very low water solubility. With the formation of stable crystalline structure, the emulsions presented gel-like behaviors and higher viscosity, which were due to the network of MG crystals.[20,21]

Meanwhile, the presence of MG crystalline structure affected the release behavior of volatiles incorporated in emulsions. Figure 2 illustrates the typical release curves of four volatile

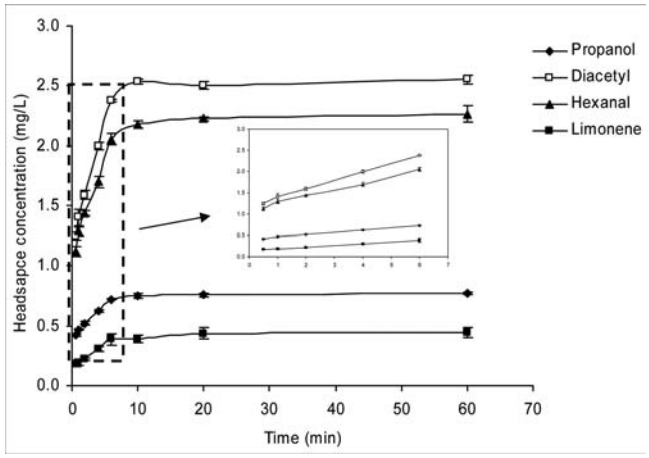

Figure 2. Representative release curves of the volatiles from MG structured emulsions (MG, 2% w/w; SO, 20% w/w). (Inset) Linear releasing range. Error bars represent standard errors.

compounds from emulsions. The release of each volatile followed a linear curve (r^2 ranging from 0.94 to 0.99) in the beginning stage (from 30 s to 6 min) and reached equilibrium within 60 min. The initial headspace concentration ($C_{initial}$) and maximum headspace concentration (C_{max}) of each volatile in different emulsion systems were compared. Figure 3A shows the $C_{initial}$ of four volatile compounds above unstructured emulsions (emulsions without MG) and of structured emulsions (emulsions with MG) on D1 and D4. It demonstrates that $C_{initial}$ values from structured emulsions were significantly lower than those from unstructured emulsions for all of the volatile compounds ($p < 0.05$), and the differentiation was higher for limonene and hexanal than for propanol and diacetyl. In the structured emulsions, the volatile compounds had lower $C_{initial}$ on D4 than on D1, because less crystalline structure was formed on D1 as indicated from the DSC result (Figure 1).

In terms of C_{max}, which represents the highest accumulated headspace concentration within the incubation period, the four volatile compounds were behaving differently (Figure 3B). All

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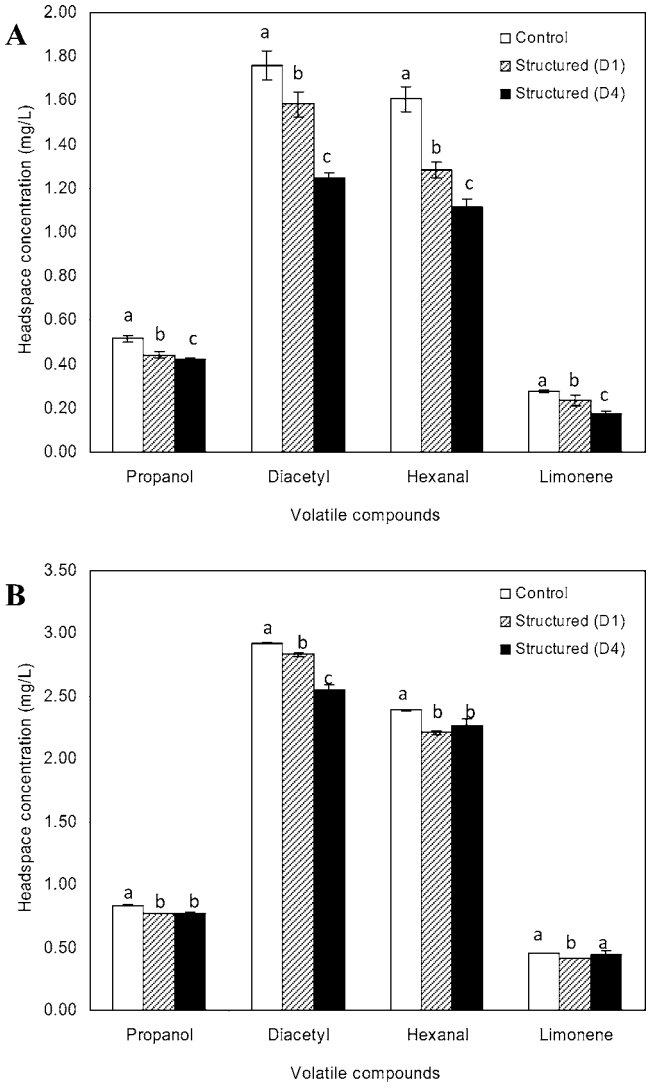

Figure 3. Initial (A) and maximum (B) headspace concentrations (mg/L) of the volatiles above MG structured emulsions (MG, 2% w/w; SO, 20% w/w) on day 1 (D1) and day 4 (D4), with those above unstructured emulsions (SO, 20% w/w) as control. Different letters above bars indicate significant differences for each volatile compound ($p < 0.05$). Error bars represent standard errors.

of the volatiles had lower C_{max} in structured emulsions than in unstructured emulsions, but the differentiations were significantly reduced compared with the $C_{initial}$ results. In the structured emulsions, diacetyl had significantly lower C_{max} on D4 than on D1, whereas limonene tended to have higher C_{max} on D4. Propanol and hexanal had unchanged C_{max} values on D4 and D1 ($p > 0.05$). The result was attributed to the polarity of the four volatile compounds,[23,24] as limonene had the highest log P value (log P = 4.6), and diacetyl (log P = −1.43) had the lowest, with propanol (log P = 0.25) and hexanal (log P = 1.78) having intermediate log P values. [31]

The above results indicated that MG structured emulsions could reduce volatile release into the headspace, in terms of both the initial burst and total release, although the magnitude varied for different volatile compounds. The findings were also reported by Phan et al.,[24] who tested volatile release from sodium caseinate-stabilized O/W emulsions structured by 0.25% MG. They found that lipophilic and amphiphilic volatiles were releasing at lower rates from structured emulsions. The maximum instant headspace concentrations of lipophilic compounds were significantly lower in structured emulsions. In that study, no significant difference in C_{max} of structured and unstructured emulsions was found, which was probably due to the lower amount of MG added.[24] To elucidate the mechanism of the delayed volatile release in MG structured emulsions, several factors can be taken into account. Inside the oil phase, the MG crystalline structure had hydrophilic domains (polar head) with large lipophilic surface (nonpolar head). This self-assembled structure could interact with both lipophilic and hydrophilic volatile compounds and, therefore, modify the affinity of volatile molecules for ingredients in the emulsion, for example, oil or emulsifier. As a consequence, partition of the volatiles from oil to water and to headspace could be affected, resulting in variation in releasing behaviors.[16,24] Moreover, the MG adsorbed at the interface could strengthen the barrier properties of the interfacial film, suggesting a more significant role in restraining the movement of volatiles from the oil to water phases.[21] Third, increased viscosity of the emulsion due to the formation of MG crystals may slow the diffusion of volatile compounds in different phases, according to the Stokes−Einstein law.[6] As stated earlier, MG was less likely located at water phase in the current system, so MG crystalline structure had a bigger influence on the release of more lipophilic volatile compounds over the release of more hydrophilic ones. Compared with the reduction in $C_{initial}$ (by 21% on average for all of the volatiles) in structured emulsions (D4), the reduction in C_{max} was much lower (by 7% on average), which indicated that MG crystalline structure had less effect on the volatile release after a longer time of incubation. It is worth pointing out that the interaction between volatile compounds and MG could also change MG crystalline structure (affect phase transition), as lipophilic moieties of volatile compounds could space the tail of MG structure and modify the packing parameter of crystals.[32] However, the volatile compounds used in this study were in low concentrations, and they were not sufficient to induce any change in MG structure.[32]As stable crystalline structure was formed on D4, we tested volatile release behavior on D4 only in the latter parts of the study.

Effect of MG Content on Volatile Release. $C_{initial}$ and C_{max} of the four volatile compounds from structured emulsions (D4) containing different amounts of MG are summarized in Table 2. Inclusion of 0.5% MG in the emulsion led to a significant decrease of the $C_{initial}$. For different volatiles, limonene had the highest reduction of $C_{initial}$ (by 24.1%), whereas propanol had the lowest (by 8.3%). When MG content was increased, a higher reduction of $C_{initial}$ was observed. The higher the amount of the crystals present, the more volatile can be adsorbed.[21] Moreover, an increased level of MG crystals can strengthen the gel property and increase the viscosity of the bulk emulsions (Table 1) and then affect volatile release.[21,33] However, the C_{max} had a trend to increase with the rise of MG content in the structured emulsions, although the structured emulsions had lower C_{max} than the unstructured emulsions. The mechanism of this finding was not well understood. It seems that oil itself was the main factor determining C_{max}, and in a system with higher MG content, the interaction between volatiles and oil was weakened.

Although volatile compounds in structured emulsions had lower $C_{initial}$ and C_{max} than those in unstructured emulsions, they were releasing at higher rates during the linear releasing stage, and the release rates were higher for emulsions with

Table 2. Initial Headspace Concentration ($C_{initial}$) and Maximum Headspace Concentration (C_{max}) (mg/L) of the Volatiles above Emulsions Varying in Oil Type, Oil Content (w/w), and MG Content (w/w) (Mean ± SD, $n \geq 3$)[a]

			propanol		diacetyl		hexanal		limonene	
oil type[b]	oil content (%)	MG[c] content (%)	$C_{initial}$	C_{max}	$C_{initial}$	C_{max}	$C_{initial}$	C_{max}	$C_{initial}$	C_{max}
SO	20	0	0.52 ± 0.02a	0.83 ± 0.01a	1.76 ± 0.06a	2.92 ± 0.01a	1.61 ± 0.06a	2.39 ± 0.01a	0.28 ± 0.01a	0.45 ± 0.01a
SO	20	0.5	0.47 ± 0.04b	0.73 ± 0.01b	1.38 ± 0.10b	2.34 ± 0.02b	1.25 ± 0.08b	1.97 ± 0.02b	0.21 ± 0.01b	0.33 ± 0.01b
SO	20	1	0.44 ± 0.06c	0.75 ± 0.02c	1.37 ± 0.14b	2.56 ± 0.05c	1.19 ± 0.11c	2.12 ± 0.05c	0.18 ± 0.02c	0.35 ± 0.02c
SO	20	2	0.42 ± 0.01d	0.77 ± 0.01d	1.24 ± 0.03c	2.56 ± 0.04c	1.12 ± 0.03d	2.26 ± 0.03d	0.18 ± 0.01c	0.44 ± 0.03a
SO	10	0	0.42 ± 0.02d	0.66 ± 0.02e	1.50 ± 0.13d	2.65 ± 0.07c	2.23 ± 0.21e	3.44 ± 0.10e	0.40 ± 0.04d	0.53 ± 0.01d
SO	10	2	0.40 ± 0.04e	0.60 ± 0.06f	1.22 ± 0.06c	2.34 ± 0.20b	2.15 ± 0.25f	3.98 ± 0.21f	0.34 ± 0.02e	0.65 ± 0.02e
MCT	20	0	0.44 ± 0.03c	0.74 ± 0.01b	1.48 ± 0.10d	2.64 ± 0.04c	1.00 ± 0.06g	1.59 ± 0.02g	0.18 ± 0.02c	0.26 ± 0.01f
MCT	20	2	0.44 ± 0.04c	0.73 ± 0.03b	1.42 ± 0.13b	2.56 ± 0.10c	0.97 ± 0.01g	1.63 ± 0.06g	0.14 ± 0.01f	0.22 ± 0.01g

[a]Within a column, values with different letters are significantly different ($p < 0.05$). [b]SO, soybean oil; MCT, medium-chain triglyceride. [c]MG, monoglyceride.

higher MG contents (Figure 4). One possible reason is that the difference in volatile concentration between headspace and bulk

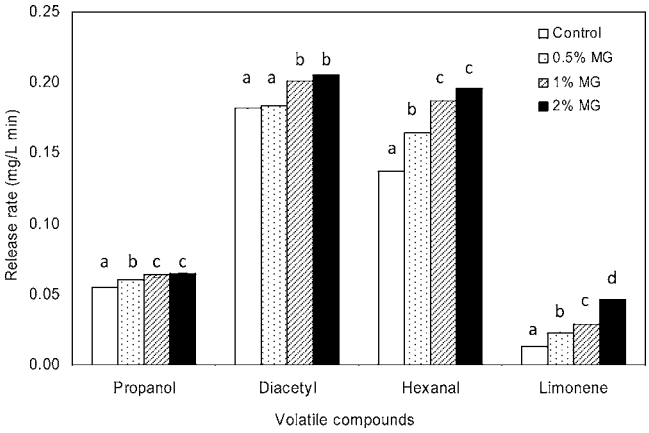

Figure 4. Release rates of the volatiles from MG structured emulsions (SO, 20% w/w) varying in MG contents compared with those from unstructured emulsion as control (SO, 20% w/w). Different letters above bars indicate significant differences for each volatile compound ($p < 0.05$). Error bars represent standard errors.

emulsion was higher for structured emulsions after the initial burst (lower $C_{initial}$), which drove volatile to the headspace more rapidly above structured emulsions. According to the penetration theory, under nonequilibrium conditions the driving force for mass transfer across interface would be the difference in volatile concentrations between the bulk emulsion and headspace.[34] An exception to the above conclusion was propanol, which had significantly the same release rate in all of the emulsions ($p > 0.05$), probably because of its high water solubility.

Table 1 shows that increase of MG content was able to produce emulsions with smaller droplet size, because MG was acting in the role of emulsifier. An earlier study reported that emulsifier mixture (MG and Tween 20 in this study) can reduce interfacial tension to a higher content than a single emulsifier used, which can facilitate the formation of smaller droplets.[17] With regard to the effect of droplet size on volatile release, controversial conclusions were found in the literature. Some studies reported that smaller droplets can accelerate volatile release because of shortened transportation radius,[4,35] whereas others argued that smaller droplets with larger interfacial area can absorb more emulsifier and then slow volatile release.[1,36] However, the movement of volatile compounds between dispersed phase and continuous phase was generally thought to be very fast,[34] especially when droplet size was reduced to the submicrometer range. Therefore, it may be difficult to find any difference in volatile release from two emulsions with different droplet sizes but at the same size scale.[11]

Effect of Oil Content on Volatile Release. $C_{initial}$ and C_{max} of the four volatiles from emulsions with lower oil content (10% w/w) are presented in Table 2. When the oil content was reduced from 20 to 10%, both $C_{initial}$ and C_{max} increased for limonene and hexanal but decreased for propanol and diacetyl, even in the presence of MG crystalline structure. This was because in the oil-reduced emulsions lipophilic compounds had relatively higher concentration in the oil phase, whereas hydrophilic compounds had relatively lower concentration in the water phase, which led to the opposite modification of the

release of the four volatiles.[1,8,37] Compared with the unstructured emulsions, the structured emulsions had much bigger increases of volatile release for limonene and hexanal when the oil content was reduced. Although the $C_{initial}$ was still lower in the structured emulsions than in the unstructured emulsions, the C_{max} was much higher ($p < 0.05$). This suggested that the release-decreased effect of MG crystalline structure was weakened in the oil-reduced systems, which, on the other hand, showed the large influence of oil content on the release of lipophilic volatile compounds. Compared with emulsions with 20% oil content (18% SO + 2% MG or 20% SO), the difference in the effective oil content between the structured emulsions (8%) and unstructured ones (10%) was magnified in fat-reduced systems, the effect of which outweighed the effect of the MG crystalline structure. Second, lower oil content inhibited the formation of gel-like property due to the reduced droplet concentration, which may also impair the function of the MG crystalline structure.[33] Correspondingly, the release rates of limonene and hexanal in structured emulsions with 10% oil were higher than those in emulsions with 20% oil content (Figure 5).

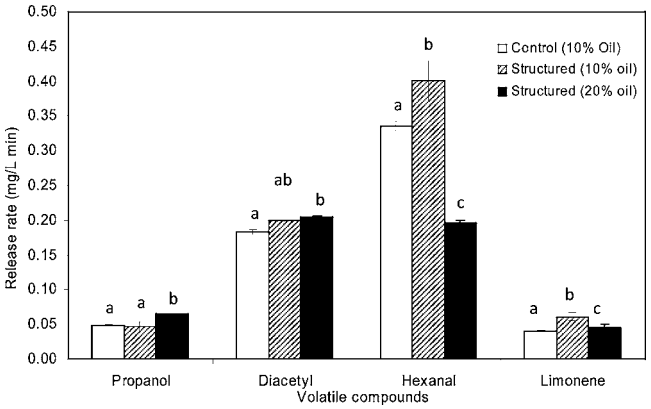

Figure 5. Release rates of the volatiles from MG structured (2% w/w) emulsions varying in SO contents compared with those from unstructured emulsion (SO, 10% w/w) as control. Different letters above bars indicate significant differences for each volatile compound ($p < 0.05$). Error bars represent standard errors.

Effect of Oil Type on Volatile Release. Medium-chain triglycerides (MCTs) are medium-chain (8−10 carbons) fatty acid esters of glycerol. They are popular in the functional food industry and are widely used as solvents for fragrances. MCT is more hydrophilic than soybean oil (SO), so it was assumed that emulsions with MCT would have higher release of more lipophilic compounds.[13] Nevertheless, both $C_{initial}$ and C_{max} of the four volatiles were significantly lower in MCT emulsions than in SO emulsions in most cases ($p < 0.05$), and headspace concentrations of the two lipophilic compounds were more affected (Table 2). Furthermore, release rates of the volatiles from MCT emulsions were lower than those from SO emulsion (Figure 6). Similar results were found by Rabe et al.,[11] who reported that lipophilic volatile compounds had higher release from emulsions containing oils with average carbon number (CN) of C14 or C16 than from miglyol-in-water (average CN of C9) emulsions. Another study reported no influence on volatile release when replacing milk fat (C16 and C18) with MCT in emulsion.[13] It seemed that lipophilicity of different oils was not the only factor that influenced the affinity of volatiles

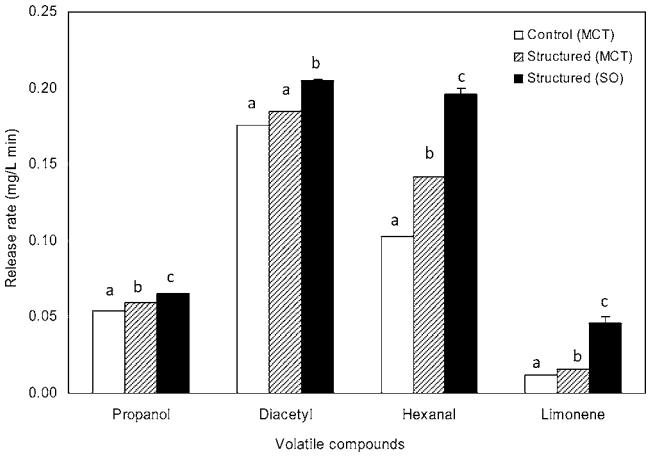

Figure 6. Release rates of the volatiles from MG structured (2% w/w) emulsions varying in oil types (SO or MCT, 20% w/w) compared with those from unstructured emulsion (MCT, 20% w/w) as control. Different letters above bars indicate significant differences for each volatile compound ($p < 0.05$). Error bars represent standard errors.

for the oils, or the affinity had already been so high that reduction in lipophilicity of the oil did not show any effect on it. From a structural point of view, the lower $C_{initial}$ and C_{max} in MCT emulsions can be related to the higher molar fraction of the oil and high saturation level of MCT. Rabe et al.[11] prepared emulsions with the same molarity of the oil phase of C16 and C9, but differing in the mass fraction, and they did not observe any significant difference in volatile release. In the current emulsion systems, with the same amount of oil added, the molarity of MCT was higher than that of SO. Second, MCT was made up of saturated fatty acids, whereas SO contained high levels of monounsaturated and polyunsaturated fatty acids. Previous studies found that volatile release was slower and of lower intensity from a system with more saturated fat than a system with more unsaturated fat.[23,38] As neither SO nor MCT was crystallized in the current system, it was suggested that different saturation levels of oils may influence MG crystalline structures in the emulsions and then influence volatile release. Also, oils varying in nature had different capacities to penetrate into the liquid crystalline phase.[39]

Interestingly, in MCT emulsions the difference in the headspace concentrations of propanol and diacetyl between structured emulsions and unstructured emulsions was very small, which was not the case in SO emulsions. This result could be attributed to the higher affinity of the two compounds for MCT, and the release behavior of these two volatile compounds was less modulated by MG crystalline structure.

Partition Coefficients of the Volatile Compounds. On the basis of the static headspace analysis, air−emulsion partition coefficients ($K_{A/E}$) of the four volatile compounds in the emulsions were calculated (Table 3). $K_{A/E}$ indicates the affinity of the volatile compounds for the emulsion matrix. With the same amount of volatiles added, limonene had the lowest $K_{A/E}$ value in all of the emulsions, whereas diacetyl and hexanal had the highest. It generally followed the polarity principle, as volatiles with lower log P values tended to partition more into the water phase and then to the headspace above the O/W emulsions.[6,23] Furthermore, volatile compounds with higher vapor pressures were likely to distribute more to the headspace. An exceptional case was hexanal, which is more nonpolar

Table 3. Air−Emulsion Partition Coefficients ($K_{AE} \times 10^4$) of the Volatiles in O/W Emulsions Varying in Oil Type, Oil Content (w/w), and MG Content (w/w) (Mean ± SD, $n \geq 3$)[a]

oil type[b]	oil content (%)	MG[c] content (%)	propanol	diacetyl	hexanal	limonene
SO	20	0	0.99 ± 0.01a	2.89 ± 0.01a	2.86 ± 0.01a	0.51 ± 0.01a
SO	20	0.5	0.87 ± 0.01b	2.30 ± 0.02b	2.34 ± 0.03b	0.38 ± 0.01b
SO	20	1	0.89 ± 0.02c	2.52 ± 0.05c	2.52 ± 0.06c	0.40 ± 0.02c
SO	20	2	0.92 ± 0.01d	2.52 ± 0.04c	2.70 ± 0.06d	0.50 ± 0.04a
SO	10	2	0.71 ± 0.08e	2.32 ± 0.25d	4.92 ± 0.26e	0.74 ± 0.02e
MCT	20	2	0.87 ± 0.04b	2.52 ± 0.10c	1.93 ± 0.07f	0.24 ± 0.02f

[a]Within a column, values with different letters are significantly different ($p < 0.05$). [b]SO, soybean oil; MCT, medium-chain triglyceride. [c]MG, monoglyceride.

(lower vapor pressure as well) than propanol, but it had a significantly higher $K_{A/E}$ value.

In most cases, volatile compounds had lower $K_{A/E}$ in structured emulsions than in unstructured emulsions. However, in oil-reduced SO emulsions, hexanal and limonene had significantly higher $K_{A/E}$ in structured emulsions. Either increase of MG contents or reduction of oil contents in the structured emulsions can significantly increase $K_{A/E}$ of hexanal and limonene, due to the weakened interaction between volatiles and oil. However, these change just slightly influenced the $K_{A/E}$ values of propanol and diacetyl. Additionally, $K_{A/E}$ can be significantly reduced by changing the oil from SO to MCT, especially for hexanal and limonene. These results suggested that $K_{A/E}$ values of volatiles with higher lipophilicity were more sensitive to the change in oil compositions in the structured emulsions.

This work presented the potential application of MG self-assembled structure to control volatile release from emulsions. The results demonstrated that structured emulsions can reduce the amount of volatile released to the headspace, more dominantly for the lipophilic compounds. For the initial burst of volatiles, MG crystalline structure can well modulate the release, whereas for the total release, which was largely dependent on oil content and oil type, the modulation was relatively weak. Therefore, when MG self-assembled structure is used to control volatile release, the nature and content of the oil phase, as well as the volatile properties, should be well considered. Meanwhile, the targeted release profile of the products, for example, a weak initial burst of volatile or a prolonged release time when consumed, should always be taken into consideration.

AUTHOR INFORMATION

Corresponding Author

*Phone: +353 25 42468. Fax: +353 25 42340. E-mail: song.miao@teagasc.ie.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

MG, monoglyceride; $C_{initial}$, initial headspace concentration; C_{max}, maximum headspace concentration; SO, soybean oil; MCT, medium-chain triglyceride; $K_{A/E}$, partition coefficient between air and emulsion; CN, carbon number; DSC, differential scanning calorimetry; PdI, polydispersity index

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