Volatile Release from an Emulsion: Headspace and In-Mouth Studies

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The headspace concentrations of three esters above solutions containing emulsified lipids were more resistant to dilution by a stream of gas than those above water alone. The effect was greatest for ethyl octanoate, and least for ethyl butyrate, with ethyl hexanoate showing intermediate behavior. This correlated with their solubility in the lipid fraction of the emulsion. Headspace analysis (comparing the emulsion with water) underestimated the release of the esters during consumption. The ratios observed between water and emulsion systems were different for the maximum breath concentration compared with headspace analysis. The emulsion appears to have acted as a reservoir for volatile release, counteracting the effects of sample dilution by saliva.

Keywords: Emulsion; APCI; API; nosespace; MS Nose

INTRODUCTION

Lipid is one of the key components of food that has a strong effect on the release of aroma, particularly in flavor systems containing hydrophobic compounds (*1* and *2*). Systems containing lipid can be studied in vitro, however, the data generated may not reflect aroma behavior during consumption. Upon consumption, processes such as dilution and phase inversion can occur; in addition, the lipid may change from the solid to the liquid form if it passes through its melting point during the course of experimentation.

Numerous methods have been used for the study of the effects of lipids on volatile release including static equilibrium headspace (3 and 4), dynamic headspace systems designed to measure rates of release (5-8), sensory analysis (9), studies of in vivo release (10 and 11), and theoretical modeling (12).

The behavior of lipids, as characterized by these different approaches, has provided a major insight into the effects of lipid on flavor. However, it is difficult to compare the methods with each other (such as static and dynamic headspace) because of differences between the systems studied. The results presented in the current paper are from a study of an emulsion at concentrations of less than 20 g/L (which should minimize matrix structure effects) and using a range of techniques (static headspace, dynamic headspace, and in vivo studies) in an attempt to monitor volatile behavior and determine the relationship between the different analytical approaches.

MATERIALS AND METHODS

Chemicals. Tricaprylin (C8 triglyceride), ethyl butyrate (99% purity), ethyl hexanoate (99% purity), and ethyl octanoate (99% purity) were obtained from Sigma-Aldrich (Poole, UK). Gum arabic, citric acid, and potassium sorbate were obtained from Fischer Scientific (Loughborough, UK).

Emulsion Preparation. Gum arabic (96 g/L), citric acid (10 g/L), and potassium sorbate (25 mg/L) were dispersed in water using a high-shear blender (Silverson Machines Ltd, Chesham, UK) for 10 min before addition of the lipid (96 g/L) and a further 25 min of blending. The solution was then passed through a homogenizer (APV, Crawley, UK) three times at 4500 psi (the temperature of the homogenizer was not specifically controlled). The final emulsion had a fairly symmetrical particle size distribution: 90% of the particles were <0.44 μ m with an average particle size of 0.3 μ m (measured using a Malvern Mastersizer, Malvern Instruments, Malvern, UK). The emulsion was stored at 4 °C until used.

Solution Preparation. Solutions of the volatiles in water (2 times final concentration) were prepared by shaking with an SF1 flask shaker (Stuart Scientific, Redhill, UK). The resulting solutions were diluted (1:1) with aliquots of the emulsion preparation (96 g/L lipid) and water, to give final lipid concentrations of 0, 2.4, 4.8, 9.6, and 19.2 g/L. These were mixed overnight on an SRT2 roller bed (Stuart Scientific) before use.

APCI Analysis. Headspace or breath was sampled into a Platform LCZ mass spectrometer fitted with an MS Nose interface (Micromass, Manchester UK) at flow rates of 5 and 60 mL/min respectively (transfer line temperature 100 °C). The analytes present in the gas phase were ionized by a 4kV corona discharge (sample cone voltage 18V) in the source (50 °C) before passing into the analyzer region of the mass spectrometer. The compounds were monitored in selected ion mode using the MH⁺ ion (dwell time: headspace analysis, 2 s; in vivo studies, 0.01 s). The relative amounts of each analyte were determined by comparison of the signal intensities obtained for samples with those of a dilute solution of the volatiles in hexane, which was introduced and volatilized in the MS Nose make-up gas stream.

Volatile Partitioning Studies. Aliquots of solution (100 mL) were placed in 250-mL flasks (Schott bottle; Fischer

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Figure 1. Headspace sampling apparatus for headspace measurements using the MS Nose.

Scientific, Loughborough, UK), each fitted with a lid with three ports (Figure 1). Headspace was sampled via the central port into the MS Nose at a flow rate of 5 mL/min while nitrogen was bubbled through the sample (5 mL/min) via the inlet tube. The amount of each compound in the headspace was obtained by peak height measurement of the steady-state signal. Measurements were made on solutions containing 5 mg/L of each ester in solutions containing a range of emulsifier or emulsified lipid at 22 °C. In addition, the solutions described in the in vivo studies section were also analyzed using this method.

Determination of Partition Coefficients. Solutions of aroma compounds in oil or water (concentration 5 mg/L) were prepared using an SF1 flask shaker (Stuart Scientific), and the headspace was sampled into the MS Nose as described above. Calibration of the MS Nose (see section on APCI analysis) allowed estimation of the gas-phase concentration, which was divided by the concentration of the compounds in the solution to produce the air/oil or air/water partition coefficients.

Dynamic Headspace Dilution Analysis. Dynamic headspace dilution analysis was performed using the methods developed by Baek (*13*) and Marin and co-workers (*14*). Samples of solutions (100 mL, containing 5 mg/L of each ester) were placed in 123-mL Schott bottles fitted with lids in a similar configuration to that shown in Figure 1, except that the inlet tube terminated in the headspace such that the headspace would be diluted. Following connection of the sampling port to the MS Nose a valve was opened allowing 70 mL/min of nitrogen to be introduced into the flask (via the inlet tube). A small proportion of the gas was sampled into the MS Nose (5 mL/min) and the excess left the flask via the outlet tube.

In Vivo Studies. Two panelists were instructed to inhale, consume a 7-mL aliquot of solution from a spoon (place in mouth and swallow), and exhale (via the nose) into a "T" piece mounted onto the end of the MS Nose transferline. The third port of the T piece served as an outlet for excess breath. Several exhalations were studied after sample consumption, such that the changes in breath volatile concentration (nosespace) could be followed over time.

Three solutions were tested: water containing 5 mg/L of each ester, a 19.2 g/L lipid emulsion containing 5 mg/L of each ester. and a 19.2 g/L lipid emulsion solution containing 15 mg/L ethyl butyrate, 100 mg/L ethyl hexanoate, and 80 mg/L ethyl octanoate. The latter solution was intended to produce headspace concentrations of the aroma compounds closer to those observed above a 5 mg/L solution in water. The amount of ethyl octanoate was, however, reduced because of concerns over solubility during sample preparation.



Figure 2. The effect of emulsified lipid concentration on the headspace concentration of three esters expressed relative to water. The continuous lines are calculated values of K_{ae} from eq 1 and the partition coefficients in Table 1; the points are the values determined experimentally. Each value is based on one measurement.

RESULTS AND DISCUSSION

Volatile Partitioning Studies. Many methods have been proposed for the study of volatile partitioning and the determination of the air/water partition coefficient; many of these have limitations which can result in error, such as volatile absorption by syringes (for a discussion see *15*). One of the main criteria used in these experimental methods is that the signal for the analyte in the gas-phase reach a steady state indicative of equilibrium, or near equilibrium (*16* and *17*), and it is this steadystate signal that is used to determine the partition coefficient.

Our method is based on the headspace method used by Guyot et al. (16) in which equilibrium in the sample flask is maintained by bubbling incoming gas (to replace gas removed from the flask) through the test solution. Using the MS Nose, gas-phase samples can be continuously removed directly from the sample flask into the mass spectrometer, via a deactivated fused-silica tube. This eliminates the use of syringes, or traps, which may result in the loss of analyte, while allowing continuous monitoring of the headspace signal. The sampling flow rate used was 5 mL/min, which was small by comparison with the headspace volume (150 mL), and it was selected to minimize disruption or dilution of the headspace during analysis. In addition, the gas introduced into the flask (to compensate for losses) was bubbled through the solution, in an attempt to further minimize headspace disruption. Once the steady-state signal maximized, it appeared to be reasonably stable, decreasing by <5% over a period of 10 min (data not shown). Subsequent calibration allowed the determination of the absolute gas-phase volatile concentration, which could then be divided by the concentration of the volatile in the liquid phase to determine the partition coefficient. Air/water (Kaw) partition coefficients measured by Marin et al. using gas phase APCI analysis (14) were found to correlate closely with theoretical estimates of K_{aw} , strongly suggesting that such a steadystate system is close to its thermodynamic equilibrium.

The headspace concentration of volatiles above aqueous solutions containing emulsions is dependent upon their partitioning between the air, water, and oil phases, as well as the fractions of oil and water present (*3*). Consequently, the headspace concentration changes as the relative proportions of oil and water are varied. Adding the emulsion to the aqueous volatile system gave different results for each of the three esters. Figure 2 shows the equilibrium headspace concentration above

Table 1. Observed Air/Oil (K_{ao}) and Air/Water (K_{aw}) Partition Coefficients for Ethyl Butyrate, Ethyl Hexanoate, and Ethyl Octanoate

| compound | Kao | K _{aw} |
|-----------------|-------------------------------------|--|
| ethyl butyrate | 2.1×10^{-4} | 4.0×10^{-2} |
| ethyl octanoate | $4.9	imes10^{-6}$ $5.6	imes10^{-6}$ | $4.0	imes10^{-2}$ $2.0	imes10^{-2}$ |

emulsion samples expressed relative to water samples, so that the behavior of all three esters can be easily compared. Ethyl butyrate showed the smallest decrease in headspace concentration as the lipid concentration increased, with ethyl octanoate showing the greatest differences. These changes are consistent with those expected on the basis of their air/water (K_{aw}) and air/ oil (K_{ao}) partition coefficients (Table 1), which reflect the differences in the chain length of the acid component of the esters.

The air/emulsion partition coefficients (K_{ae}) for the lipid emulsions were estimated for each lipid concentration using the relationship from Buttery and co-workers (3), with

$$K_{\rm ae} = 1/(F_{\rm w}/K_{\rm aw} + F_{\rm o}/K_{\rm ao}) \tag{1}$$

where $F_{\rm w}$ and $F_{\rm o}$ are the fractions of water and oil, respectively. These calculated values were comparable with those observed by equilibrium headspace analysis (Figure 2). This suggested that the emulsifier was not influencing $K_{\rm ae}$ significantly.

Dynamic Headspace Dilution Analysis. The dynamic headspace dilution apparatus used in these studies determined the capacity of volatiles to maintain their headspace concentration, while the headspace was continuously diluted by a stream of nitrogen. The initial conditions prior to dilution were very close to those of the static headspace equilibrium (as described in the section on volatile partitioning studies) which served as a reference point. The factors affecting the behavior of volatile compounds in a gas dilution system were characterized by Marin and co-workers (18). They found that the principal factor affecting the changes in the headspace volatile concentration was K_{aw} . The headspace concentration for compounds with high K_{aw} values (e.g., 1×10^{-2}) decreased rapidly when the headspace was diluted, compared to those of compounds with low $K_{\rm aw}$ values (e.g., 1×10^{-5}).

With the introduction of emulsion into the aqueous phase, a new equilibrium headspace concentration is achieved, a value dependent on the oil fraction. An increase in the oil fraction results in a decrease in K_{ae} which should (according to the model) increase the capacity of a compound to maintain its headspace concentration. This, however, assumes that the change in the mobility of the volatiles in the aqueous phase is minimal as the emulsion concentration changes. For this to happen, it is necessary for the volatiles to partition between the lipid and the aqueous phase during the course of the experiment.

Ethyl butyrate showed the least change in its headspace concentration as the oil fraction was increased (Figure 2). Consequently, only the solutions containing 9.6 and 19.2 g/L emulsified lipid showed any difference under dynamic headspace conditions when compared with ethyl butyrate in water (Figure 3). The relative differences between the K_{aw} and K_{ae} values were much larger for ethyl hexanoate than they were for ethyl butyrate. This compound exhibited a greater stability in its headspace concentration during gas-phase dilution, with clear differences for the 19.2, 9.6, and 4.8 g/L lipid emulsions and water. The greatest effect, however, was observed for ethyl octanoate, which showed the largest difference between $K_{\rm aw}$ and $K_{\rm ae}$ (Figure 2). This compound showed a capacity to maintain a higher headspace concentration during gas-phase dilution for samples containing as little as 2.4 g/L lipid emulsion.

These results clearly demonstrate that emulsions can enhance the stability of the headspace volatile concentration during gas phase dilution. Haahr et al. (19) found that the rate of release of volatiles under dynamic headspace conditions was initially very high for water compared to emulsion. However, the rate of release for water decreased substantially thereafter, consistent with a decrease in the partitioning of volatiles into the headspace. In contrast, the emulsions showed a steady progressive release of volatiles over time (although the overall absolute rates of release were lower), indicative of a much more stable volatile headspace concentration. Voilley et al. (20) also found that the rate of volatile loss (nonanone content) from an emulsion system was much lower than the rate of volatile loss from a purely aqueous system. These results are further evidence of the stabilizing effect of emulsions as observed by dynamic headspace dilution analyses.

It is clear that volatiles were able to readily partition between the lipid and water phases of the sample. This effect (greater stability of the volatile concentration in the headspace) could affect orthonasal aroma delivery during the consumption of beverages containing cloud emulsions, and other systems with higher lipid concentrations (e.g., mayonnaise). This hypothesis is consistent with the findings of McNulty (9), who found that the headspace above emulsion solutions rapidly reached equilibration with a half-life of less than 15 s. Changing the composition of emulsions may substantially affect the rate of partitioning of aroma compounds between lipid and water phases, and the MS Nose dynamic headspace dilution method could be used to characterize these differences.

Modeling Dynamic Headspace Dilution Analysis Curves. The models describing the dynamic partitioning of volatile compounds into the headspace above aqueous solutions upon dilution can be developed using either convection- or diffusion-based models to describe the liquid phase (18). The convection approach gives a simple overall model of the release, and was able to describe the behavior of the esters in water in these experiments. However, as the emulsion content of the system was increased, the convective model was unable to accurately describe the changes in headspace volatile concentration during dilution (Figure 4). It was, however, possible to model these changes using the more complex diffusion-based model. The coefficients used in both models (diffusion coefficient and liquid masstransfer coefficient) did not decrease substantially compared to those of water, which strongly suggested that there was no significant structure effect of the emulsion within the range of systems studied. This type of behavior would be expected of a homogeneous phase, which is not unexpected given the low lipid concentrations (<20 g/L) and small particle size of the emulsion (average 0.3 μ m).

The key difference between the two models is the way volatile concentration from the gas interface to the bulk of the solution is considered to behave. In the convective



Figure 3. Normalized (100%) time-course profiles for dynamic headspace dilution measurements of ethyl octanoate (a), ethyl hexanoate (b), and ethyl butyrate (c). Emulsified lipid concentrations: 0, (*); 2.4, (\Box); 4.8, (\blacksquare); 9.6, (\bigcirc); and 19.2, (\bullet) g/L. Each curve is the average of two replicates.

model the equivalent gradient of concentration (film theory) near the surface is considered to be constant, and the concentration inside the bulk liquid has a uniform volatile concentration, which can become progressively depleted upon dilution of the headspace. Whereas, in the diffusion-based model, a concentration gradient is continuously increasing from the surface to the bulk phase (1.5 to 3 mm), with the highest volatile concentration in the bulk phase remaining constant. The fact that a diffusion-based model was required for the emulsions is possibly due to the poor mobility of the relatively large emulsion droplets within the aqueous phase, when compared with that of the volatiles themselves.

The point at which a convective model failed to describe the behavior of aroma compounds and it was necessary to use the diffusive model (for an example see Figure 4) was different for each of the esters. The curves for ethyl octanoate required diffusion-based models for all emulsion concentrations to obtain a good fit between the experimental data and the theoretical curve. Whereas

the headspace dilution behavior of ethyl butyrate was adequately described by convective models for all of the lipid concentrations studied. Ethyl hexanoate exhibited intermediate behavior, requiring the convective model for lipid concentrations lower than 10 g/L and the diffusion model thereafter. The point at which the transition from a convective to a diffusive model was necessary (for each compound), corresponded to an emulsion concentration in which less than 10% of the volatile was dissolved in the aqueous phase and more than 90% of the volatile was dissolved in the lipid itself. Further work will be necessary to determine whether this is a specific phenomena common to all aroma compounds or to just the three esters used in these studies. Whatever the model, the dynamic partitioning of the volatiles between the air and emulsion phases could be closely related to the static equilibrium partition coefficients determined for each emulsion.

In Vivo Studies. The effects observed for the headspace system showed the potential for reequilibration of aroma compounds in a three phase system over a



Figure 4. Ethyl hexanoate dynamic headspace dilution analysis above a 19.2 g/L lipid emulsion (*) modeled using either a convection model, with a liquid mass transfer coefficient of 1×10^{-6} m/s (dashed line), or a diffusion model, with a diffusion coefficient of 1.2×10^{-9} m²/s (continuous line). All other modeling parameters were fixed (mass transfer coefficient = 3×10^{-2} ; surface area = 2×10^{-3} m²; volume of liquid in flask 1×10^{-4} m³; gas flow rate through cell = 1×10^{-6} m³s⁻¹; gas volume in flask = 1×10^{-4} m³; layer thickness = 0.25×10^{-3} m).



Figure 5. Headspace concentrations and breath I_{max} values $(\pm \text{ SD})$ from emulsions normalized to the concentrations observed for the water samples (100%). The solutions contained 5 mg/L ethyl octanoate (a), ethyl hexanoate (b), and ethyl butyrate (c), in water (clear), or 19.2 g/L lipid emulsion (striped). The means are the result of 3 headspace and 6 nosespace replicates.

period of several minutes. The eating process is typically much shorter, and, in the case of solutions, may be just a few seconds. The effect of the presence of emulsions in-mouth was tested using esters dissolved in water, or the 19.2 g/L lipid emulsion, which were consumed while the breath volatile concentration was monitored (the headspace concentration of the esters above these solutions was also determined). The values for the breath maximum volatile concentration (I_{max}) and headspace concentration were normalized against the values for water (100%) for ease of comparison (the two sets of data were ca. 100 to 500-fold different in magnitude).

Ethyl butyrate in the 19.2 g/L lipid emulsion gave a breath I_{max} equivalent to 70% of that observed for the totally aqueous system. This was not expected on the basis of the headspace data, in which the ethyl butyrate signal for this emulsion system was only 30% that of

the water system (Figure 5). The same pattern of results was observed for both ethyl hexanoate and ethyl octanoate, but the differences were even greater. Ethyl octanoate at 5 mg/L was barely detectable in the headspace above the emulsion in comparison with that above the water, but produced a breath $I_{\rm max}$ for the emulsion equivalent to 40% of that observed for the totally aqueous sample.

An accurate comparison of the differences between the ratios for the headspace concentrations and the breath $I_{\rm max}$ concentrations was not possible for the 5 mg/L solutions, because of the low concentrations of volatiles in the headspace for the longer-chain esters. An additional set of 19.2 g/L lipid emulsions were prepared with an increased concentration of the esters, and the headspace and breath $I_{\rm max}$ concentrations were determined. These values were normalized against those obtained for 5 mg/L of each ester in water which served as a reference between the headspace and nosespace systems. This concentration (5 mg/L) was chosen because it was within the solubility limits of the compounds, and it should produce a headspace concentration.

The ratio between the normalized breath I_{max} and headspace values for ethyl butyrate was determined as follows. The peak height observed for ethyl butyrate in the headspace above the emulsion (containing 15 mg/L ethyl butyrate) was 1.5 times higher than that observed for the headspace above water (containing 5 mg/L ethyl butyrate), whereas this ratio was a factor of 3.3 during consumption. By dividing the nosespace ratio (3.3) by the headspace ratio (1.5), the extent to which greater release had occurred during consumption could be determined (in this case a factor of approximately 2). This was carried out for all three esters, which showed that ethyl butyrate, ethyl hexanoate, and ethyl octanoate were present at 2, 5, and 25 times higher concentrations in the breath (respectively) than expected on the basis of the headspace analysis.

Clearly there are substantial differences between the headspace and in vivo systems. This finding is consistent with the sensory data presented by de Roos and Wolswinkel (21). They found that the changes in concentration required to reformulate flavors in milk (compared with water) were different for odor (headspace or orthonasal sampling) when compared with taste (nosespace or retronasal sampling). They added 113 times as much linalyl acetate to the milk to give it the same odor as an aqueous solution, but added only 8.8 times as much linalyl acetate to the milk to give it the same taste. The most likely explanation of these findings is that they were dependent on release rather than any other perceptual differences caused by the matrix.

APCI studies of the release of volatiles into the breath conducted by Malone and co-workers (*22*) also found that the breath volatile concentration was higher than expected when consuming emulsions. No static headspace data were presented; however, on the basis of their oil/water partition coefficients for ethyl hexanoate (631) and heptanone (72) the headspace concentration above a 10 g/L lipid emulsion should decrease by 86 and 42% (respectively) when compared with that of water. However, the breath volatile concentration of ethyl hexanoate and heptanone decreased by only 60 and 16%, respectively. Despite the fact that the eating protocol in their experiments differed substantially from



Figure 6. Normalized (100%) theoretical maximum volatile concentrations above solutions of ethyl octanoate in water or 19.2 g/L lipid emulsion following dilution of the solutions. The values were calculated using the partition coefficients in Table 1 and the equations from Buttery et al. (*3*).

ours (i.e., chewing the sample rather than instantly swallowing it) their results showed the same trend. In addition, they also studied emulsions with 300 g/L lipid; these also showed much greater breath volatile concentrations than expected on the basis of the oil/water partition coefficient. Ethyl hexanoate and heptanone should have both exhibited a maximum breath concentration less than 5% of that observed for aqueous samples; however, the levels were 10 and 38% respectively (compared with water). It therefore appears that this phenomenon is not just restricted to systems with a low lipid concentration, but also occurs at higher lipid concentrations.

The headspace dilution analysis demonstrated the capacity for reequilibration of the aroma compounds between the lipid and water phases of the emulsion system, and it is likely that these processes are responsible for the differences observed during consumption. McNulty (9) showed that dilution of samples by saliva in-mouth could lead to differences in release between water and emulsions. Dilution of an aqueous solution results in a decrease in volatile concentration and hence a decrease in the maximum potential gas-phase concentration above it because this is dependent on K_{aw} . Dilution of the emulsion also reduces the volatile concentration in the system, however, dilution also alters K_{ae} which is dependent on the oil fraction. The change in K_{ae} reduces the overall effect of the decrease in volatile concentration and maintains a higher potential gas-phase concentration (Figure 6).

The headspace data showed that the K_{aw} for ethyl octanoate was 30 times higher than the K_{ae} for the 19.2 g/L lipid; however, the difference in the breath I_{max} values was only a factor of 2.6 (Figure 5). If these differences were due to the dilution of the emulsion and subsequent changes in K_{ae} a 19-fold dilution of the sample would be needed. The estimated dilutions required to account for the breath volatile concentrations of ethyl hexanoate and ethyl butyrate were factors of 10 and 8, respectively. The differences between the esters may reflect experimental variation in the in vivo studies; it does, however, appear that substantial dilution of the sample could have occurred during consumption (possibly affecting only a small fraction of the sample residing in the throat after swallowing).

One of the other parameters measured for the breath volatile release curves was the extent of volatile persistence. Values for this were obtained by dividing the intensity of the volatile in the second exhalation after swallowing by the intensity of the first. No significant differences were observed between any of the samples (data not shown). This may be attributed to the fact that the system reequilibrated rapidly upon consumption and there was little further potential for reequilibration because of the high mobility (convective mass transport) of the volatile in this homogeneous emulsion.

The fact that no differences in persistence were observed when the esters were consumed in emulsions rather than water may also have resulted from the dilution of the sample following ingestion. Upon dilution, assuming no large variation in mobility (mass transfer coefficient), the K_{ae} increases and approaches K_{aw} , consequently, any differences resulting from the presence of the emulsion would have decreased and in this instance reached the point where they were no longer significant.

Other emulsion systems with slower equilibration dynamics (i.e., systems containing solid rather than liquid lipid) may be more likely to show smaller effects on I_{max} and greater effects on persistence (diffusion in a heterogeneous phase). Persistence of volatile compounds in the breath has been observed to increase as the lipid concentration of a food system increased (*11* and *22*). However, these differences were only apparent when the lipid concentration used in our experiments.

CONCLUSIONS

Because of its versatility, the MS Nose can be used to characterize the effect of lipids on volatile release by headspace, dynamic headspace dilution analysis, and during consumption. This shows that the extent to which a compound interacts with an emulsion system affects its concentration in the gas phase above the solution and its capacity for reequilibration between the aqueous and lipid phases in-mouth during consumption.

Emulsions could be used to increase the loading of hydrophobic volatile compounds in hydrophilic food systems (beyond their normal limits of solubility). Subsequent dilution of the emulsion upon consumption would result in a change in the partition coefficient and a release of some of the volatile dissolved in the lipid fraction in vivo, thereby delivering the flavor to the consumer.

ACKNOWLEDGMENT

We are grateful to representatives of Procter & Gamble, Firmenich, and the Scientific Council of the French Embassy for their helpful discussions regarding this research.

LITERATURE CITED

- Overbosch, P.; Afterof, W. G. M.; Haring, P. G. M. Flavor release in the mouth. *Food Rev. Int.* **1991**, *7*, 137–184.
- (2) de Roos, K. B. How lipids influence food flavor. Food Technol. 1997, 51, 60-62.
- (3) Buttery, R. G.; Guadagni, D. G.; Ling, L. C. Flavour Compounds: volatilities in vegetable oil and oil-water mixtures. Estimation of odor thresholds. *J. Agric. Food Chem.* 1973, *21*, 198–201.
- (4) Landy, P.; Courthaudon, J.-L.; Dubois, C.; Voilley, A. Effect of interface in model food emulsions on the volatility of aroma compounds. *J. Agric. Food Chem.* **1996**, *44*, 526–530.
- (5) Desamparados, S.; Bakker, J.; Langley, K. R.; Potjewijd, R.; Martin, A.; Elmore, S. Flavour release of diacetyl from water, sunflower oil and emulsions in model systems. *Food Qual. Prefer.* **1994**, *5*, 103–107.
- (6) Roberts, D. D.; Acree, T. E. Effects of heating and cream addition on fresh raspberry aroma using a retronasal aroma simulator and gas chromatography olfactometry. *J. Agric. Food Chem.* **1996**, *44*, 3919–3925.
- (7) Odake, S.; Roozen, J. P.; Burger, J. J. Effect of saliva dilution on the release of diacetyl and 2-heptanone from cream style dressings. *Nahrung–Food* **1998**, *42*, 385– 391.
- (8) Springett, M. B.; Rozier, V.; Bakker, J. Use of fiber interface direct mass spectrometry for the determination of volatile flavor release from model food systems. *J. Agric. Food Chem.* **1999**, *47*, 1125–1131.
- (9) McNulty, P. B. Flavour release elusive and dynamic. In *Food Structure and Behavior*; Blanshard, J. M., Lillford, P., Eds.; Academic Press: London, 1987; pp 245–258.
- (10) Haring, P. G. M. Flavour Release from Product to perception. In *Flavour Science and Technology*. Bessière, Y., Thomas, A. F., Eds.; John Wiley & Sons Ltd.: Chichester, U.K., 1990; pp 351–354.
- (11) Brauss, M. S.; Linforth, R. S. T.; Cayeux, I.; Harvey, B.; Taylor, A. J. Altering the fat content affects flavor release in a model yogurt system. *J. Agric. Food Chem.* **1999**, *47*, 2055–2059.
- (12) Harrison, M.; Hills, B. P.; Bakker, J.; Clothier, T. Mathematical models of flavor release from liquid emulsions. *J. Food Sci.* **1997**, *62*, 653–664.

- (14) Marin, M.; Baek, I.; Taylor, A. J. Volatile release from aqueous solutions under dynamic headspace dilution conditions. J. Agric. Food Chem. 1999, 47, 4750-4755.
- (15) Chaintreau, A.; Grade, A.; Muñoz-Box, R. Determination of partition coefficients and quantitation of headspace volatile compounds. *Anal. Chem.* **1995**, *67*, 3300–3304.
- (16) Guyot, C.; Bonnafont, C.; Lesschaeve, I.; Issanchou, S.; Voilley, A.; Spinnler, H. E. Relationships between odourous intensity and partition coefficients δ -decalactone, diacetyl and butyric acid in model emulsions. In *Flavour Science: Recent Developments.* Taylor, A. J., Mottram, D. S., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1996; pp 380–385.
- (17) Turner, L. H.; Chiew, Y. C.; Ahlert, R. C.; Kosson, D. S. Measuring vapor-liquid equilibrium for aqueousorganic systems: review and a new technique. *AIChE J.* **1996**, *42*, 1772–1788.
- (18) Marin, M.; Baek, I.; Taylor, A. J. Flavor release as a unit operation: a mass transfer approach. In *Flavor Release: Linking Experiments, Theory and Reality*, Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 153–165.
- (19) Haahr, A.-M.; Bredie, W. L. P.; Stahnke, L. H.; Jensen, B.; Refsgaard, H. H. F. Flavour release of aldehydes and diacetyl in oil/water systems. *Food Chem.* 2000, *71*, 355–362.
- (20) Voilley, A.; Espinosa Diaz, M. A.; Druaux, C.; Landy P. Flavor release from emulsions and complex media. In *Flavor Release: Linking Experiments, Theory and Reality*; Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 142–152.
- (21) de Roos, K. B.; Wolswinkel, K. Nonequilibrium partition model for predicting flavour release in the mouth. In *Trends in Flavour Research*; Maarse, H., Van der Heij, D. G., Eds.; Elsevier Science: Amsterdam, 1994; pp 15– 31.
- (22) Malone, M. E.; Appelqvist, A. M.; Goff, T. C.; Homan, J. E.; Wilkins, J. P. G. A novel approach to the selective control of lipophilic flavor release in low fat foods. In *Flavor Release: Linking Experiments, Theory and Reality*, Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 212–227.

Received for review July 10, 2000. Revised manuscript received November 16, 2000. Accepted November 20, 2000. Financial support for this research was provided by Procter & Gamble, Firmenich, and the Scientific Council of the French Embassy.

JF000853A