JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2003,** *51,* 189−195 **189**

Experimental and Modeling Studies Showing the Effect of Lipid Type and Level on Flavor Release from Milk-Based Liquid Emulsions

DEBORAH D. ROBERTS,* PHILIPPE POLLIEN, AND BRIGITTE WATZKE

Nestlé Research Center, Vers Chez les Blanc, P.O. Box 44, 1000 Lausanne 26, Switzerland

The purpose of this work was to study two key parameters of the lipid phase that influence flavor release—lipid level and lipid type—and to relate the results to a mass balance partition coefficient-based mathematical model. Release of 10 volatile compounds from milk-based emulsions at 10, 25, and 50 °C was monitored by 1-min headspace sampling with a solid-phase microextraction fiber, followed by GC-MS analysis. As compared to the observations for milk fat, changing to a lipophilic lipid (medium-chain triglycerides, MCT) and adding a monoglyceride-based surfactant did not influence the volatiles release. However, increasing the solid fat content was found to increase the release. At 25 °C, and even more so at 10 °C, concurrent with an increase in their solid fat content, hydrogenated palm fat emulsions showed increased flavor release over that observed for emulsions made with coconut oil, coconut oil with surfactant, milk fat, and MCT. However, at 50 °C, when hydrogenated palm fat emulsions had zero solid fat content, there was no difference in flavor release from that observed for milk fat emulsions. Varying milk fat at nine levels between 0 and 4.5% showed a systematic dependence of the release on the lipid level, dependent on compound lipophilicity. Close correlations were found between the experimental and model predictions with lipid level and percent liquid lipid as variables.

KEYWORDS: Partition coefficients; oil; model; interaction

INTRODUCTION

The ability of the fat phase in a food product to absorb aroma compounds has a significant impact on the performance of a given flavoring. In numerous model emulsions (*1*, *2*) and more complete foods (*3*, *4*), the differences in headspace concentration (*5*) and the resulting sensory intensity (*6*) due to discrete modifications of the lipid level are well noted. Reviews of the effect of lipids on flavor release show their importance in overall flavor (*7*, *8*).

In a previous study with milk, an experimental design directly changing the levels of milk solids nonfat and milk fat showed that the lipid phase was the main component influencing flavor compound volatility (*9*). Although evidence of protein or lactose binding to lipophilic compounds was seen as skim milk concentration increased, this effect was no longer present after the addition of 1.3% lipid. Other studies also showed that in the presence of 1% or greater lipid, aroma compound binding by β-lactoglobulin was insignificant (*10*). The objective of the present study was to investigate how changing the lipid type and level could influence this effect. In the first study of different lipid types, less lipophilic lipids were compared to milk fat to see if they would absorb lipophilic aroma compounds to a lesser degree. Additionally, lipids containing higher solid fat contents were tested at different temperatures in order to test a hypothesis that only lipids in the liquid form could absorb flavor compounds.

In addition to the factors tested in this study, the interface could also influence aroma compound volatility. Several studies show significant differences based on the emulsifier (*11*), yet others show little difference (*12*, *13*), depending on the compound studied.

Several mathematical models have also been published that relate the theoretical headspace concentration to the amounts in food emulsions, based on partition coefficients (*14*−*17*). An excellent review of physiochemical models of flavor release was published by de Roos (*18*). A further purpose of the study described herein was to thoroughly test a mass balance partition coefficient-based mathematical model using numerous flavor compounds and concentrations.

MATERIALS AND METHODS

Preparation of Milk-Based Emulsions. *Materials.* The following materials were used for preparing milk-based emulsions: skim milk powder containing 0.57% lipid, 34.7% true protein, 52.7% lactose, and 95.5% milk solids nonfat, coconut oil (Morgia, Lyss, Switzerland), surfactant based on mono- and diglyderides (with minimum 60% monoglycerides, Cremodan 60, Danisco, Brabrand, Denmark), milk fat (Corman, Goe-Dolhain, Belgium), medium-chain triglycerides (C8:C10 60:40, Delios V, Impag, Zurich, Switzerland), hydrogenated palm fat

* Corresponding author (telephone 41 21 7858172, fax 41 21 7858554, E-mail Deborah.Roberts@rdls.nestle.com).

10.1021/jf025646k CCC: $25.00
Published on Web 11/28/2002

45/46C (Florin AG, Muttenz, Switzerland), 2,3-diethyl-5-methylpyrazine, and 2-isobutyl-3-methoxypyrazine (both from Pyrazine Specialities Inc., Atlanta, GA). All other aroma compounds were from Aldrich (Steinheim, Germany).

Method. Skim milk powder and water were mixed and heated to 60 °C. The mixture was pre-emulsified at 60 °C using a hand-held Ultraturrax for 3 min at 8000 turns/min using the medium-size dispersing head. During this pre-emulsification, the lipid was added in small portions. With stirring, the mixture was then homogenized with three passes using a Buchi homogenizer (Flawil, Switzerland) at 65 °C. The milk sample was cooled on ice and then stored in a refrigerator until use. Lipid globule size distributions were verified to be similar to those of commercial milk by using a Malvern Mastersizer (Malvern, UK). The samples had between 86 and 96% of the lipid globules under 1 μm and a D[3,2] (sum of volume/sum of surface) between 0.33 and 0.53. In the lipid type study, only the lipid source varied, and the lipid percentage (wt/vol) in the final product, after mixing with the aroma solution, was 1.38%. In the lipid level study, the grams of milk fat and water were varied to have lipid percentages (wt/vol) in the final product of 0, 0.02, 0.1, 0.2, 0.36, 0.61, 0.89, 1.38, and 4.58. The samples contained 2.9% milk solids nonfat, which includes 1% protein.

Throughout the Materials and Methods, lipid percentage is expressed as grams per 100 mL. However, in the Modeling sections of the Results and Discussion, in order to meet the requirements of the model, lipid percentage is expressed as a volumetric percentage (see eq 1).

Solution Preparation. The concentrations of aroma compounds were chosen so that they were in the linear quantification range of the solid-phase microextraction (SPME) fiber. The aroma compounds were dissolved in water with extended vial shaking and checked for complete solubilization by looking at the solution surface. Milk solutions (400 mg, as prepared above) were added to silylated 2-mL glass vials. Aqueous aroma solution (400 mg) was added and mixing was done without inverting the vial. The final concentrations in the samples (in mg/L) were 2,3-butanedione, 10; pyridine, 10; guaiacol, 10; 2,3-diethyl-5-methylpyrazine, 10; 1-octen-3-ol, 2; ethylguaiacol, 10; 2-isobutyl-3-methoxypyrazine, 2; β-damascenone, 2; 2-pentylfuran, 0.1; and limonene, 0.1.

Headspace Analysis by SPME GC-MS. A minimum time of 2 h was determined for equilibration, during which the samples were placed on an orbital shaker (KS 250, IKA-Werke, Staufen, Germany) at 200 turns/min. The temperature for preparation and equilibration was 25 °C for all samples except for the lipid type study. In the lipid type study, samples were equilibrated and analyzed at the indicated temperature. Samples to be analyzed at 25 and 50 °C were prepared at 25 °C. Samples to be analyzed at 10 °C were prepared at 10 °C and also at 25 °C for comparison. After equilibration, the headspace of the samples was sampled using a Varian 8200cx autosampler. A HP 5890 gas chromatograph (GC) equipped with a HP 5971 mass spectrometric (MS) detector was used. A SPME fiber was inserted into the headspace and allowed to equilibrate for 1 min exactly. This time was chosen so that the extraction would be from the headspace and not from the sample. The fiber used was polydimethylsiloxane/divinylbenzene with 65 μm thickness. It was placed into the injection port, containing a 0.75-mm-i.d. liner, of the GC for 5 min at 250 °C. During the first 3 min of desorption, the purge was off, and the last 2 min, with purge on, further cleaned the fiber. Full desorption of the fiber was confirmed. GC separation with MS detection in SIM mode was used for quantification of the aroma compounds [DBWAX, J&W, 30 m; 0.25 mm i.d., 0.25 mm film, 0.8 mL/min, constant flow (5 psi at 40 °C)]. All samples were prepared in the vials and analyzed in triplicate.

Triplicate blank milk analyses for each milk type without aroma compounds were also run to verify that the compounds followed were not present at substantial quantities in the milk. The only compound that was found in the milk was 2,3-butanedione, at maximum 0.5% levels of the added aroma compounds. There were no other compounds coeluting at the same time as these compounds.

Four series of SPME analyses were run: (1) lipid level study, (2) lipid type study at 10 °C, (3) lipid type study at 25 °C, and (4) lipid type study at 50 °C. A separate SPME fiber was used for each series. A balanced sample order was used, in which the first replicate of each milk type was analyzed, and then the second, and last the third. During each series, a water reference, containing compounds dissolved at the same concentration as in the milk, was analyzed in triplicate. The release of each compound in water was used as a benchmark for the release of that compound in the emulsion. The peak area of each compound in milk (H_M) was expressed relative to the peak area of that compound in water (H_w) using the formula $(H_M/H_w) \times 100$.

Measurement of Partition Coefficients. The aroma compounds were selected because they had a large range of oil−water partition coefficients. Values for the oil−water partition coefficient from sunflower oil were from Pollien and Roberts (*19*), who used a shake-flask method based on quantification in the two phases using solid-phase microextraction. The air−water partition coefficients were measured according to Chaintreau et al. (*20*), using a stainless steel sampling cell at three different concentrations. Values obtained for oil−water and air−water partition coefficients, respectively, were 2,3-butanedione, 0.37, 0.0011; guaiacol, 9.3, 0.00026; 2,3-diethyl-5-methylpyrazine, 31, 0.0005; 4-ethylguaiacol, 46, 0.00066; 1-octen-3-ol, 48, 0.0031; and 2-isobutyl-3-methoxypyrazine, 280, 0.0032). Values for the oil−water partition coefficient were pyridine, 0.59; β-damascenone, 1230; 2-pentylfuran, 3733; and limonene, 4815. It was not possible to analyze some compounds for their air−water partition coefficient due to difficulties in obtaining stable results. Extrapolated values were used: pyridine, 0.0009; β-damascenone, 0.012; 2-pentylfuran, 0.0343; and limonene, 0.044. As determined later, the air−water partition coefficient has almost no influence on the results of the model (**Figure 3**); thus, the accuracy of these values is not important.

Statistical Analysis. Analysis of variance ($\alpha \leq 0.05$) was used to determine the existence of significant differences among samples combined with a multiple comparison test (Fisher's LSD, $\alpha \leq 0.05$) to determine which samples were significantly different from the others.

Solid Fat Content. The solid fat content of the lipids studied was measured according to IUPAC method 2.150 6.2.2.2.

RESULTS AND DISCUSSION

Mathematical Model of Lipid's Influence Based on Partition Coefficients. The mathematical model developed used the relationships first cited in the work of Buttery et al. (*17*). According to this relationship, a flavor compound in an oil and water mixture and in a closed system with air will equilibrate and distribute itself between these mixture phases and air in a constant ratio at a given temperature. The flavor mass is redistributed in these different phases according to the different partition coefficients:

$$m_I = m_A + m_W + m_O$$

$$K_{AW} = \frac{C_A}{C_W} \qquad K_{OW} = \frac{C_O}{C_W}$$

with m_A, m_W, and m_O referring to respectively the flavor mass at equilibrium in the air, water, and oil phases. K_{AW} and K_{OW} are the partition coefficients between air and water and between oil and water, respectively.

As a first hypothesis in the model, we disregard any irreversible ab- or adsorption between flavor compounds and any mixture component such as lactose or milk protein. We allowed each flavor compound, with an initial mass m_I, only three possible environments in which to distribute: air, water, and oil phases. All non-lipid phases in the samples are counted as "water".

Experimentally, we measured the flavor compound released at equilibrium in the sample headspace. The peak area of each compound in milk (H_M) was expressed relative to the peak area of that compound in water (H_w) using the formula $(H_M/H_w) \times 100$. In terms of the model, this is equivalent to eq 1. The release of the compounds from emulsions, $(m_A)f_O$, was expressed relative to the release of the compound at the same concentration

Table 1. Relative Headspace Concentration of Milk-Based Emulsions at 1.36% Lipid Content Using Different Lipids (100 = Headspace above Compounds in Water)[a]

	experiment at 10 °C					experiment at 25 °C					experiment at 50 °C	
compound[c]	hydrogenated palm fat	coconut oil (CO)	CO with surfactant	milk fat	MCT[b]	hydrogenated palm fat	coconut oil (CO)	CO with surfactant	milk fat	MCT[b]	hydrogenated palm fat	milk fat
2,3-diethyl-5-methylpyrazine	131 a	114 ab	105 ab	113 ab	90 b	106 a	87 b	79 b	85 b	88 ab	75 a	63 a
1-octen-3-ol	96 a	77 b	67 b	75 b	48 c	86 a	56 b	51 b	56 b	50 b	50 a	44 b
ethylguaiacol	94 a	69 b	55 b	54 b	36 c	72 a	50 b	45 b	54 b	43 b	48 a	47 a
2-isobutyl-3-methoxypyrazine	82 a	38 b	31 b	34 b	19 c	49 a	22 b	20 b	22 b	20 b	24 a	21 b
β-damascenone	33 a	8.6 b	6.2 c	6.7 bc	4.8 c	13 a	4.5 b	3.9 b	4.6 b	3.6 b	4.9 a	4.4 b
2-pentylfuran	6.6 a	1.5 b	1.2 c	1.3 bc	0.74 d	4.67 a	1.41 b	1.25 bc	1.36 bc	1.16 c	4.9 a	3.7 a
limonene	4.1 a	0.77 b	0.59 cd	0.71 bc	0.41 d	2.9 a	0.93 b	0.76 b	0.91 b	0.87 b	3.6 a	3.0 a
approximate solid fat content	95	80	75	50	0	70	0	0	10	0	0	0

[a] Different letters note significant differences for one compound at one temperature across emulsion types. Within this group, compounds bearing different letters show statistically significant differences from each other. [b] Medium-chain triglycerides. [c] Emulsions and water showed no significant differences in release of 2,3-butanedione, guaiacol, and pyridine.

in water, $(m_A)_{water}$. Different oil volumic fractions (f_O) were inserted into the model to give the predictions based on lipid amount; the prediction is independent of lipid type. The development of this model is included in the Supporting Information.

In the frame of the model, this aroma release compared to water case is expressed as

$$\frac{(m_A)_{f_O}}{(m_A)_{water}} = \frac{\left(\frac{V_A}{V_E}\right)_{f_O}\left(K_{WA} + \left(\frac{V_A}{V_W}\right)_{water}\right)}{\left(\frac{V_A}{V_W}\right)_{water}\left(K_{WA}(f_O K_{OW} + f_W) + \left(\frac{V_A}{V_E}\right)_{f_O}\right)} \quad (1)$$

with V_A, V_W, and V_E the volumes occupied by the air, the water, and the emulsion phases, respectively; f_W is the water volumic fraction ($f_W + f_O = 1$), and K_{WA} is the partition coefficient between water and air.

With this model, we assumed that the SPME headspace analysis using a 1 min sampling time is close to a static headspace equilibrium measurement, as previously shown (*21*). The closeness of the experimental results to the predicted results indicate that this assumption is valid. The experimental results will now be described and linked with the model.

Effect of Lipid Type. Medium-chain triglycerides (MCT) were chosen because they are among the least lipophilic lipids. The MCT used has short-chain fatty acids of C8−C10 length, which are half the length of normal fatty acids. As milk fat absorbs nonpolar flavor compounds due to its lipophilicity, it was postulated that lipids with less lipophilicity would absorb less of these nonpolar aroma compounds. In another sample, a surfactant of mainly monoglycerides was added to coconut oil triglycerides in an attempt to lower the surface tension on the fat globules by its emulsifying effect. This was done to change the fat globule interface properties. However, the triglyceride content only changed from 99 to 95%.

Table 1 shows the comparison at 25 °C when all lipids were 90−100% liquid, except for hydrogenated palm fat, which was about 30% liquid. Coconut oil with a surfactant added and MCT did not show a difference in flavor compound absorption from the results for milk fat and coconut oil. This indicates that the lipophilicity of all of the lipids is at such a large level that reductions in the length of the fatty acid (MCT) do not affect flavor release, nor does a supposed change in the surface tension at the globule surface.

Previous literature studies show evidence that the saturation level of the lipids could play a role in flavor compound absorption: with stearine, a more saturated fat, the release was shown to be slower and of lower intensity than the release with olein (a more unsaturated fat) (*22*). Within the range of lipids used in this study, the saturation of the lipid plays a role in how it influences the solid fat content, which is the driving factor.

Influence of Solid Fat Content at Different Temperatures. Another hypothesis tested was a dependence on the lipid's physical state: flavor compounds can only penetrate fat globules that are in a liquid state. McNulty and Karel (*23*) showed decreases in the oil-to-water transfer rate upon increasing the solid fat index. Thus, if a fat is continuously in a solid state, there will be no interactions with the aroma compounds, and the effective concentration of the aroma compounds in the aqueous phase will be higher. Thus, the release is expected to be higher when solid fat rather than liquid fat is present. Maier (*24*) also showed that the sorption of aroma compounds was greater in liquid triglycerides than in solid triglycerides. Indeed, in this study, the effect of solid fat content on flavor compound absorption was significant.

Table 1 shows the volatiles release results from emulsions at different temperatures, where the lipids had a range of solid fat contents. At 50 °C, both lipids tested are 100% liquid. The differences observed at lower temperatures between the lipids are negligible at 50 °C. At 25 °C, hydrogenated palm fat showed a higher release than the other lipids. This fat had 70% solid fat at this temperature and so would be expected to have a higher release. At 10 °C, greater differences in solid fat content existed between the different lipid types. In these cases, the samples were prepared and analyzed at 10 °C, meaning that the flavor compounds only contacted lipid in its state at 10 °C. As at 25 °C, the hydrogenated palm fat emulsion had a higher release the others. However, greater differentiation is observed between the other lipid types, with MCT showing the lowest release. Among coconut oil, coconut oil with surfactant, and milk fat, some differences are observed for the most lipophilic compounds where coconut oil has a slight edge in release, perhaps due to its higher solid fat content.

The relationship between the solid fat content and the flavor released can be also illustrated by taking one type of lipid and analyzing it at several temperatures. All compounds in hydrogenated palm fat show the trend of increasing release upon increasing solid fat in the emulsion (**Table 1**).

MCT is an oil that is 100% liquid at both 10 and 25 °C. The only significant differences found between the two temperatures are with the two most lipophilic compounds (2-pentylfuran and

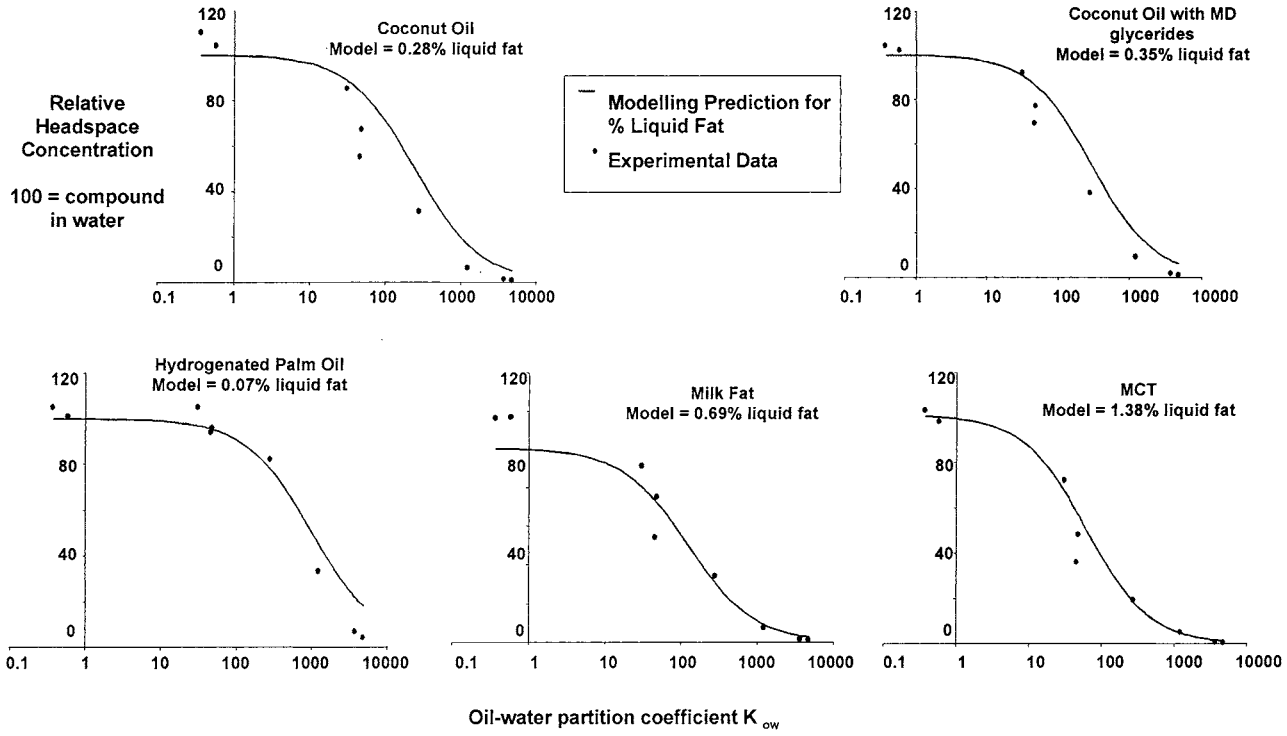

Figure 1. Graphs showing proximity of model to experiments, assuming that only liquid lipid influences flavor absorption: compound release at 10 °C for systems containing 1.38% lipid. Pyridine is not included due to an impurity in the samples.

Table 2. Modeling Fits of Lipid Content to Experimental Results at 10 °C When Liquid Lipid Content Varied (Values Shown Are % Lipid in wt/vol)

lipid type	actual % lipid	liquid lipid (%)	best modeled % lipid
hydrogenated palm fat	1.38	0.07	0.16
coconut oil	1.38	0.28	0.44
coconut oil with surfactant	1.38	0.345	0.69
milk fat	1.38	0.69	0.69
MCT	1.38	1.38	1.38

limonene). At both temperatures, the lipid significantly absorbs the compounds.

One theory that has been postulated is that the chain length of the fatty acids influences the absorption of volatile compounds, where longer chains absorb greater amounts (*22*). The MCT oil used has a 60:40 C8:C10 fatty acid ratio. The other lipids have a mix, where coconut oil has a larger percent of C12 and C14, and milk fat and hydrogenated palm fat have more C16 and C18. However, this study shows that a range of currently used lipids that have different fatty acid compositions did not differ in release when in a liquid state. Reductions in compound absorption are seen only when at least 50% of the lipid is in a solid state.

Modeling can be used to see how good a predictor the liquid lipid content is of the experimental release values. In **Figure 1**, the modeled flavor release curves were developed on the basis of a hypothesis that only lipid in the liquid state influences flavor release. In the cases of milk fat and MCT, the predicted release, based on the liquid lipid content, matches very well the experimental results. For the others, the "best-fit" lipid content is shown in **Table 2**. These results shows that percentage of liquid lipid is a close predictor of the flavor release. For all values, the best-fit model more closely matched the liquid lipid content than the total lipid content.

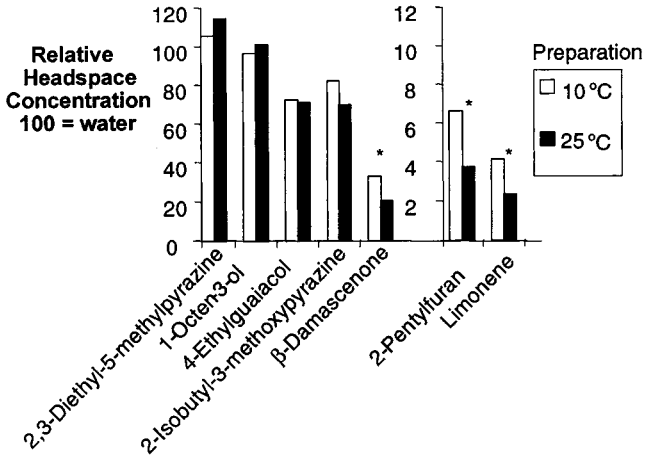

Figure 2. Influence of temperature preparation on flavor release from milk-based emulsions made with hydrogenated palm fat at 10 °C. The asterisk notes statistically significant differences.

The history of the contact between the lipid and the aroma compounds can influence the results obtained. For instance, the samples from the study conducted at 10 °C were prepared and analyzed at 10 °C. However, if the samples were prepared at room temperature and then analyzed at 10 °C, the results may be different: the flavor compounds could have been absorbed by the lipid when it was in a liquid state at room temperature, and then entrapped in the solid fat at 10 °C, hence lowering the release. This experiment was performed, and the results are shown in **Figure 2**. For the most lipophilic compounds, a difference was observed that depended on the preparation method. These compounds showed a higher release when the lipid was always held at 10 °C and was mainly in a solid state. When the lipid was prepared at 25 °C, these compounds probably migrated into the lipid phase that was solidified at 10

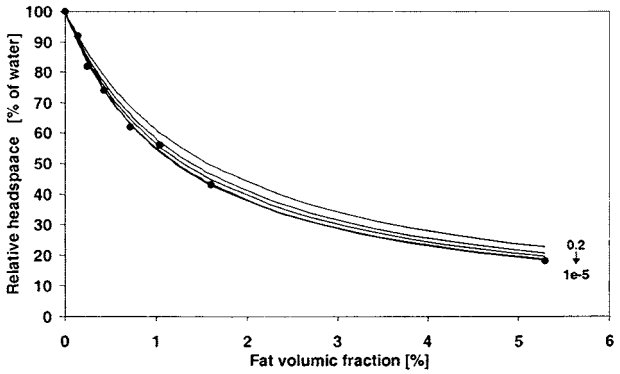

Figure 3. Theoretical influence of K_{AW} on the release of 4-ethylguaiacol. Different lines represent modeled release for different K_{AW} values. Points are experimental results.

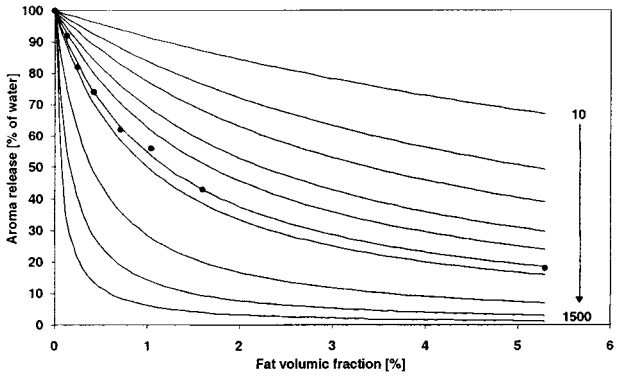

Figure 4. Theoretical influence of K_{OW} on the release of 4-ethylguaiacol. Different lines represent modeled release for different K_{OW} values (10, 20, 30, 45, 60, 83.4, 100, 250, 600, and 1500, from top to bottom). Points are experimental results.

°C, resulting in a reduced headspace concentration due to entrapment in the solid fat.

Modeling of Lipid Level on the Basis of Partition Coefficients. The oil−water partition coefficients were determined experimentally. For some of the compounds, the determination of K_{AW} was not successful with the technique employed. We linearized the relationship between the measured partition coefficients in order to extrapolate the missing K_{AW} partition coefficients from the measured K_{OW} ones. This approach is not recommended for prediction but was done for the purpose of the exercise. As is shown below, the exact value of K_{AW} has little influence on aroma release.

From previous experiments at 30 °C, the measured K_{AW} ranged from 1×10^{-4} to almost 2×10^{-2}. To establish the real impact of K_{AW} on the headspace flavor released after equilibrium, we calculated the behavior of some flavor compounds with K_{AW} values ranging arbitrarily from 1×10^{-5} to 2×10^{-1}. As can be seen in **Figure 3**, the impact of K_{AW} in the screened range is negligible, and all values, especially the true one, came close to the experimental data. On extending the K_{AW} range to higher values (higher than actually found for aroma compounds), an increasing influence of the air−water partition coefficient on the aroma release starts to be evident when K_{AW} reaches at least 1% of the K_{OW} value.

The model (cf. eq 1) relies mainly on K_{OW} values, lipid volumic fraction, and the volumes occupied by oil, water, and air phases. As can be seen in **Figure 4**, K_{OW} is of prime importance, as evidenced by the large differences in curves obtained upon its variation.

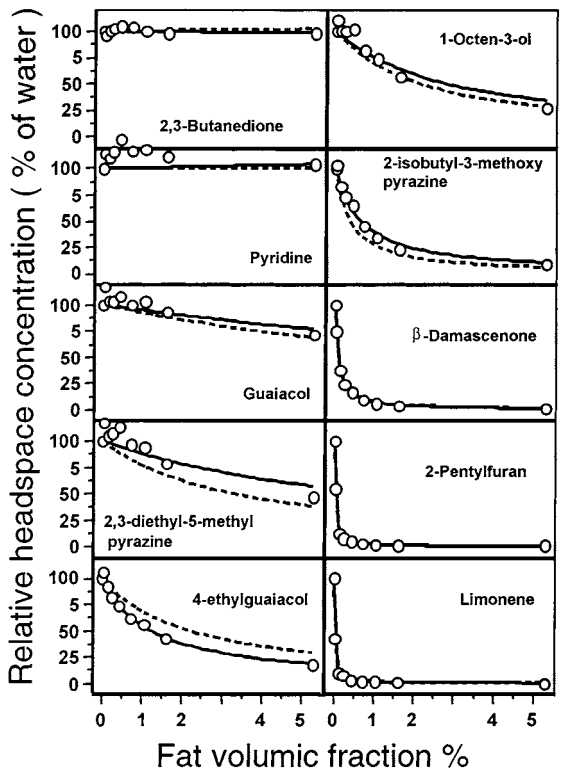

Figure 5. Compound aroma release as a function of lipid content. Points are experimental results, and the solid line is the model's best-fit solution with the data. The dashed lines are the model's predicted results based on the compounds' measured partition coefficients.

In general, the compounds tested here seem to exhibit minimal effect of protein binding, as the assumption that the system would follow predicted release from a basic oil-in-water emulsion was valid. However, if other compounds were tested that exhibit strong binding to sodium caseinate, such as 2-nonanone, deviations such as those seen by Voilley et al. (*25*) may have been seen. Molecular explanations for the interactions observed between the lipid phase and flavor compounds have been postulated by (*26*). They show FT-IR evidence for the presence of hydrogen bonds between linoleic acid and 1-octen-3-ol and 2,5-dimethylpyrazine.

Figure 5 shows the simulated flavor release of the 10 studied aroma compounds versus lipid level in the emulsion. The aroma compounds vary greatly in their sensitivity to the lipid level. The more lipophilic the compound, the lower the amount of lipid needed to reduce its headspace concentration. For example, the most lipophilic compound, limonene, is greatly reduced in volatility with very small amounts of lipid. However, larger amounts of lipid are required to reduce the volatility of more polar guaiacol. For each compound, there is a different range of lipid contents where flavor release is most greatly influenced, and this can be effectively modeled. This can be useful, for instance, if a known flavor impact compound is being targeted. The lipid content can be adjusted to optimize the flavor release of the compound. Similar results have been found with equilibrium headspace concentration (*27*) and in-mouth release analysis (*28*), showing the relationship between lipid content and release for various compounds

In comparing the calculated release curves to the experimental points, we see a good correspondence for almost all compounds. For the most hydrophilic compounds, some values are over 100 but not statistically different from 100, showing the variance in the method. The compound that seems to have a difference

Table 3. Measured and Adjusted Values Measuring Compound Lipophilicity

compound	K_{OW}[a]	K_{OW} in milk[b]	K_W[c]
2,3-butanedione	0.37	0	0.5
pyridine	0.59	2	4
guaiacol	9.3	15	9
2,3-diethyl-5-methylpyrazine	31	29	54
4-ethylguaiacol	46	101	83
1-octen-3-ol	48	52	426
2-isobutyl-3-methoxypyrazine	280	186	269
β-damascenone	1230	955	617
2-pentylfuran	3733	2972	3311
limonene	4815	2874	8128

[a] Measured by shake-flask method using sunflower oil. [b] Adjusted by best fit of experimental points. [c] Compound lipophilicity was determined on the basis of its retention time on a reversed-phase HPLC (*19*).

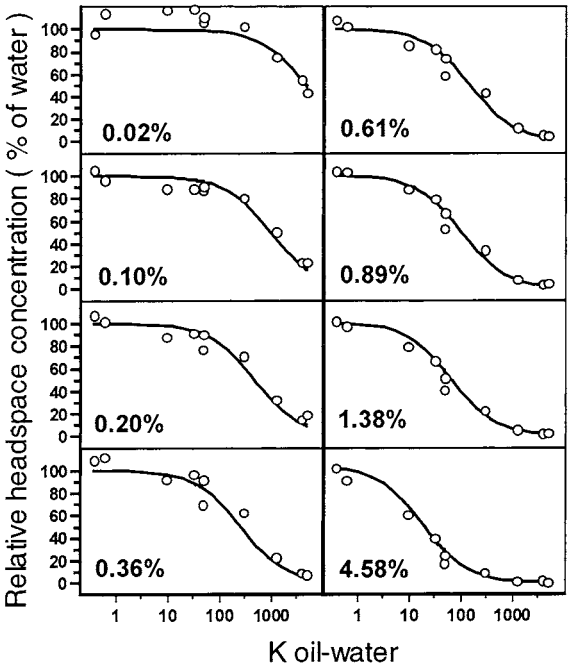

Figure 6. Aroma compound release as a function of K_{OW} (measured from sunflower oil–water) of the compound. Points are experimental results with milk samples of different fat contents (between 0.02 and 4.58%). Lines are the model's predicted results based on the compounds' measured partition coefficients.

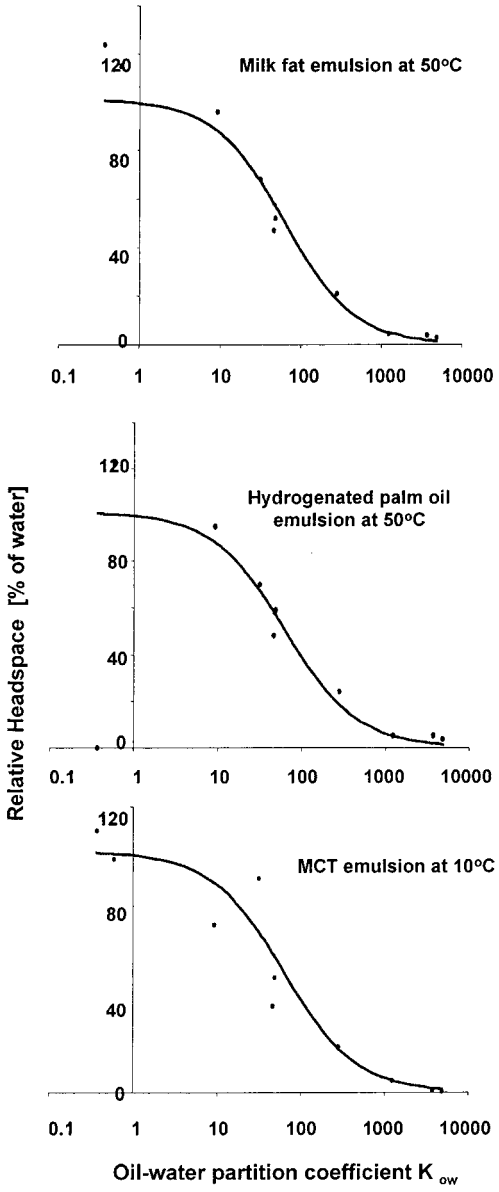

Figure 7. Correspondence of modeling (solid lines) and experimental results (points) from 1.38% lipid emulsions, showing the fit at various temperatures.

from the modeling is 4-ethylguaiacol, which shows a lower release than that modeled on the basis of its oil−water partition coefficient. It should be noted that these K_{OW} values were obtained in an oil (sunflower oil) which is not the milk fat used in the experiments.

As K_{OW} is such a major parameter and the measured values were from sunflower oil in a bulk phase, we tried an approach to "adjust" the values to those which give the best fit with the experimental release results. The best-fit values are shown in **Figure 5** and **Table 3**. In fact, this best-fit K_{OW}, called K_{OW} in milk, is another way, perhaps more realistic, of determining the true value for milk fat in milk emulsions. The differences between the measured K_{OW} values, the adjusted K_{OW} values, and the K_W lipophilicity values are not negligible for some of the compounds. Although the correct value for the model is the K_{OW} value, the use of this model with the K_W lipophilicity values would still give an indication of the headspace aroma released at equilibrium.

In another way of visualizing the lipid's influence, **Figure 6** shows the release versus partition coefficient K_{OW} for various lipid levels. From the graph, one can see that, depending on the lipid content of the sample, compounds with a different range of lipophilicity will be reduced in release. The experimental points correspond excellently with the model. The reason that reduced fat foods are sometimes unbalanced in flavor can be seen easily. On going from a 5% to a 0% lipid milk emulsion, the most lipophilic compounds will be greatly increased in release, while the least lipophilic compounds will be unchanged. This verified experimental/theoretical model can thus help predict what effects a change in lipid content would have on the equilibrium headspace flavor profile.

Although most of the experiments to validate the model were performed at 25 °C, **Figure 7** shows that the model is valid for higher and lower temperatures as well, as long as the solid fat content does not change.

With 10 compounds tested that span the range of lipophilicity and with 8 lipid concentrations tested, all compared to the release in water, a thorough study was conducted. These results allow

us to conclude that the partition coefficient-based model corresponded very well to the experimental results. A significant effect of lipid level was demonstrated that depended on the lipophilicity of the aroma compound. In addition, the liquid lipid content of the sample was found to absorb aroma compounds, as samples with higher solid fat content showed higher release.

Supporting Information Available: Mathematical development of emulsion flavor release model (eq 1). This material is available free of charge via the Internet at http://pubs.acs.org.

LITERATURE CITED

(1) 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.

(2) Doyen, K.; Carey, M.; Linforth, R. S. T.; Marin, M.; Taylor, A. J. Volatile release from an emulsion: headspace and in-mouth studies. *J. Agric. Food Chem.* **2001**, *49*, 804−810.

(3) Brauss, M. S.; Balders, B.; Linforth, R. S. T.; Avison, S.; Taylor, A. J. Fat content, baking time, hydration and temperature affect flavour release from biscuits in model-mouth and real systems. *Flavour Fragrance J.* **1999**, *14*, 351−357.

(4) 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.

(5) Welty, W. M.; Marshall, R. T.; Gruen, I. U.; Ellersieck, M. R. Effects of milk fat, cocoa butter, or selected fat replacers on flavor volatiles of chocolate ice cream. *J. Dairy Sci.* **2001**, *84*, 21−30.

(6) Gwartney, E. A.; Foegeding, E. A.; Larick, D. L. The role of texture and fat on flavor release from whey protein isolate gels. In *Flavor Release*; Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 355−367.

(7) Hatchwell, L. C. Overcoming flavor challenges in low-fat frozen desserts. *Food Technol.* **1994**, *48*, 98−100.

(8) de Roos, K. B. How lipids influence food flavor. *Food Technol.* **1997**, *51*, 60−62.

(9) Roberts, D. D.; Pollien, P. Relative influence of milk components on flavor compound volatility. In *Flavor Release*; Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington DC, 2000; pp 321−332.

(10) Seuvre, A. M.; Espinosa-Diaz, M. A.; Voilley, A. Influence of the food matrix structure on the retention of aroma compounds. *J. Agric. Food Chem.* **2000**, *48*, 4296−4300.

(11) Charles, M.; Rosselin, V.; Beck, L.; Sauvageot, F.; Guichard, E. Flavor release from salad dressings: sensory and physicochemical approaches in relation with the structure. *J. Agric. Food Chem.* **2000**, *48*, 1810−1816.

(12) 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.

(13) Roberts, D. D.; Pollien, P.; Watzke, B. Flavour release from milk-based liquid emulsions: key influence of fat phase. In *Proceedings from the Weurman Symposium 2002*; Editions Tec et DOC: Paris; in press.

(14) Harrison, M.; Hills, B. P.; Bakker, J.; Clothier, T. Mathematical models of flavor release from liquid emulsions. *J. Food Sci.* **1997**, *62*, 653−658.

(15) McNulty, P. B.; Karel, M. Factors affecting flavour release and uptake in O/W emulsions. I. Release und uptake models. *J. Food Technol.* **1973**, *8*, 309−318.

(16) de Roos, K. B.; Wolswinkel, K. Non-equilibrium partition model for predicting flavour release in the mouth. In *Trends in Flavour Research*; Maarse, H., Van der Heij, D. G., Eds.; Elsevier: London, 1994; pp 15−32.

(17) Buttery, R. G.; Guadagni, D. G.; Ling, L. C. Flavor compounds: volatiles in vegetable oil and oil−water mixtures. Estimation of odor thresholds. *J. Agric. Food Chem.* **1973**, *21*, 198−201.

(18) de Roos, K. B. Physiochemical models of flavor release from foods. In *Flavor Release*; Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 126−141.

(19) Pollien, P.; Roberts, D. Use of solid-phase microextraction for measuring oil−water partition coefficients and correlation with high-performance liquid chromatographic methods for lipophilicity. *J. Chromatogr. A* **1999**, *864*, 183−189.

(20) Chaintreau, A.; Grade, A.; Munoz-Box, R. Determination of partition coefficients and quantitation of headspace volatile compounds. *Anal. Chem.* **1995**, *67*, 3303−3304.

(21) Roberts, D. D.; Pollien, P.; Milo, C. Solid-phase microextraction method development for headspace analysis of volatile flavor compounds. *J. Agric. Food Chem.* **2000**, *48*, 2430−2437.

(22) Bakker, J. Flavour interactions with the food matrix and their effects on perception. In *Ingredient Interactions: Effects on Food Quality*; Gaonkar, A. G., Ed.; Dekker: Basel, 1995; pp 411−439.

(23) McNulty, P. B.; Karel, M. Factors affecting flavour release and uptake in O/W emulsions. II. Stirred cell studies. *J. Food Technol.* **1973**, *8*, 319−331.

(24) Maier, H. G. Binding of volatile aroma substances to nutrients and foodstuffs. In *Aroma Research*; Maarse, H., Groenen, P. J., Eds.; Center for Agricultural Publishing and Documentation: Wageningen, The Netherlands, 1975; pp 143−157.

(25) Voilley, A.; Espinosa-Diaz, M. A.; Druaux, C.; Landy, P. Flavor release from emulsions and complex media. In *Flavor Release*; Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 142−152.

(26) Le Thanh, M.; Goubet, I.; Quere, J. L.; Voilley, A. Interactions between volatiles and lipids in complex systems. *J. Am. Oil Chem. Soc.* **1998**, *75*, 441−445.

(27) Schirle-Keller, J. P.; Reineccius, G. A.; Hatchwell, L. C. Flavor interactions with fat replacers: effect of oil level. *J. Food Sci.* **1994**, *59*, 813−815.

(28) Malone, M. E.; Appelqvist, I. A. M.; Golf, 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*; Roberts, D. D., Taylor, A. J., Eds.; American Chemical Society: Washington, DC, 2000; pp 212−227.

Received for review May 2, 2002. Revised manuscript received October 6, 2002. Accepted October 6, 2002.

JF025646K