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Influence of Lipid Fraction, Emulsifier Fraction, and Mean Particle Diameter of Oil-in-Water Emulsions on the Release of 20 Aroma Compounds

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The influence of compositional and structural properties of oil-in-water emulsions on aroma release was examined under mouth conditions. The lipid (0.40 and 0.65) and emulsifier fractions (0.007, 0.010, and 0.014) were varied, as well as the mean particle diameter of the dispersed phase (0.60, 0.73, 0.85, and 1.10 μm). Aroma compounds were isolated in a model mouth system and quantified by gas chromatography−mass spectrometry. Studies were carried out to separate effects on the thermodynamic and the kinetic components of aroma release using equilibrium headspace analysis to distinguish the thermodynamic component. The lipid phase of the emulsions was composed of sunflower oil and the emulsifier phase was Tween 20. The release of 20 aroma compounds was evaluated; the compounds included alcohols (1-propanol, 1-butanol, 3-methyl-1-butanol, 2-pentanol, 1-hexanol, and 2-nonanol), ketones (diacetyl, 2-butanone, 2-heptanone, 2-octanone, and 2-decanone), esters (ethyl acetate, propyl acetate, butyl acetate, and ethyl butyrate), aldehydes (hexanal, heptanal, and octanal), a terpene (α-pinene), and a sulfur compound (dimethyl sulfide). Decrease in lipid fraction and emulsifier fraction, as well as increase in particle diameter, increased aroma release under mouth conditions. Differences between groups of compounds and between compounds of homologous series with varying chain lengths were found. Changes in particle diameter had a considerable effect on the thermodynamic component of aroma release, whereas hardly any influence of the lipid fraction and emulsifier fraction was observed. Lipid fraction, emulsifier fraction, and particle diameter affected the kinetic component of aroma release, which could partially be attributed to changes in viscosity.

KEYWORDS: Aroma release; emulsifier; emulsion; particle diameter; sunflower oil

INTRODUCTION

Flavor perception occurs when flavor molecules are released from a food matrix, are transported, and come into contact with receptors in the mouth and nose. Interactions between aroma compounds and food matrix components play an important role in the perception of flavor. With the growing range of new foods available, many with lower fat formulations than the traditional foods, it is becoming increasingly important to understand the factors that affect the release of aroma compounds. Knowledge of binding behavior of aroma compounds in specific food matrixes and their rates of partitioning between different phases is of great practical importance for the flavoring of foods, and in determining the relative retention of aroma compounds during processing, storage, and consumption (*1*−*2*).

Lipids are part of most food matrixes. They modify the physical properties of foods, thereby affecting mouthfeel, appearance, and structure. Lipids may also act as flavor precursors, as a solvent for aroma compounds, and as aroma release modulators (*3*). Lipids have shown a considerable effect on qualitative, quantitative, and temporal aroma release (*4*−*5*). Bulk oils received attention in this respect (*6*−*7*). However, many natural and processed foods do not consist of bulk oils but exist either partly or wholly as emulsions (*8*). Emulsified systems are dispersions of droplets of one liquid (e.g., oil) in another liquid with which it is incompletely miscible (e.g., water). Milk, mayonnaise, salad dressings, cream, ice cream, butter, and margarine are examples of food emulsions.

Aroma release is determined by thermodynamic and kinetic factors. Thermodynamics of aroma release involve the partitioning of aroma compounds under equilibrium conditions, which determines the extent of aroma release. The rate at which equilibrium is achieved is defined by kinetic factors. The driving force of aroma release under dynamic conditions is the difference in aroma concentration in the food and the air above a food (*9*). To understand complex food systems, studies on simplified food systems are required to examine the influence of single factors on aroma release. There are indications that not only the composition of emulsions affects aroma release but that the emulsion structure should be considered as well (*10*). Although oil-in-water (O/W) or water-in-oil emulsions (W/O) seem fairly simple model systems, a number of compositional

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Table 1. Specification of Oil-in-Water Emulsions: Sample Codes, Oil Fraction (Φ_o), Emulsifier Fraction (Φ_e), Mean Particle Diameter (D_{32}), Dispersion, and Relative Viscosity[a]

sample code	Φ_o	Φ_e	D_{32} [μm]	dispersion [μm]	relative viscosity
LLL	0.40	0.007	0.60	1.46	6.0
LML	0.40	0.010	0.60	1.37	5.8
LMM	0.40	0.010	0.73	1.80	4.8
LMH	0.40	0.010	0.85	2.35	4.4
LHL	0.40	0.014	0.60	0.99	5.8
HMH	0.65	0.010	0.85	2.21	–[b]
HMXH	0.65	0.010	1.10	2.37	–

[a] Fractions calculated on mass basis. Dispersion = $D(v,0.9) - D(v,0.1)$. In sample codes first letter refers to oil fraction, second letter to emulsifier fraction, and third/fourth letter to particle diameter (L refers to low, M to medium, H to high, and XH to extra high). [b] Viscosities of samples HMH and HMXH could not be measured accurately because the method is not appropriate for non-Newtonian fluids.

and structural properties can be varied, such as the type of lipid, emulsifier, and aroma compound; the size of the lipid, water, and emulsifier fraction; the mean particle diameter; and the particle size distribution. Most studies in this area have been concerned with a few parameters and a relatively small number of aroma compounds (*11*−*12*).

The aim of the present study is to examine the influence of compositional and structural properties of O/W emulsions on aroma release. The impact of the lipid fraction, emulsifier fraction, and mean particle diameter on release under mouth conditions was determined for 20 aroma compounds. Additionally, the effect of the emulsion parameters on the thermodynamic and kinetic component of aroma release was evaluated.

MATERIALS AND METHODS

Sample Materials. The lipid phase of the emulsions was composed of commercial sunflower oil (Suma Wholefoods, Dean Clough, Halifax, UK). Distilled water was used for the water phase and Tween 20 (polyoxyethylene sorbitan monolaurate; Fluka Chemie, Buchs, Switzerland) was the emulsifying agent. The 20 aroma compounds included diacetyl, 2-butanone, ethyl acetate, 2-pentanol, hexanal, 1-hexanol, 2-heptanone, heptanal, and α-pinene, which were supplied by Aldrich (Steinheim, Germany). Dimethyl sulfide, ethyl butyrate, 2-octanone, and octanal were purchased from Merck (Hohenbrunn, Munich, Germany). 1-Propanol, propyl acetate, 1-butanol, butyl acetate, and 3-methyl-1-butanol were supplied by Lancaster (Walkerburn, UK), and 2-nonanol and 2-decanone were obtained from Fluka Chemie.

The artificial saliva consisted of $NaHCO_3$ (5.208 g), $K_2HPO_4 \cdot 3H_2O$ (1.369 g), NaCl (0.877 g), KCl (0.477 g), $CaCl_2 \cdot 2H_2O$ (0.441 g), NaN_3 (0.5 g), mucin (2.160 g), and 200,000 units of α-amylase (hog pancreas α-amylase; Fluka Chemie) in 1 L of distilled water, and was adjusted to pH 7 (*13*).

Emulsion Preparation. Sunflower O/W emulsions varying in lipid fraction (ϕ_o), emulsifier fraction (ϕ_e), and particle diameter (D_{32}) were prepared as indicated in **Table 1**, using a prototype single valve homogenizer with a cooling unit which maintained the temperature during homogenization at 20 °C. Three emulsions varying in emulsifier fraction ($\phi_e = 0.007$, 0.010, and 0.014), but with constant lipid fraction ($\phi_o = 0.40$) and mean particle diameter ($D_{32} = 0.60$ μm) were made. By modifying the energy during homogenization, O/W emulsions varying in mean particle diameter ($D_{32} = 0.60$ μm and 0.85 μm) were made with oil fractions $\phi_o = 0.40$ and 0.65, and emulsifier fraction $\phi_e = 0.010$. The two O/W emulsions with different mean particle diameters ($\phi_o = 0.40$, $D_{32} = 0.60$ μm and 0.85 μm) were mixed 1:1 v/v to obtain a third O/W emulsion ($D_{32} = 0.73$ μm). Maximum energy input resulted in emulsions with $D_{32} = 0.60$ μm for $\phi_o = 0.40$, and $D_{32} = 0.85$ μm for $\phi_o = 0.65$. The 20 aroma compounds were added to the emulsions after preparation, which resulted in a final concentration of 0.001% v/v per compound. The emulsions were stored in Erlenmeyer flasks for 12 h at 4 °C in absence of light to allow equilibration. In preliminary experiments, the procedure of adding compounds after homogenization was compared with addition of the compounds to the oil fraction prior to homogenization. No significant differences in headspace concentrations were found between the two procedures (MANOVA, $P < 0.05$).

Emulsion Characterization. A Mastersizer laser diffractometer (model S Ver. 2.15, Malvern Instruments, Malvern, UK) was used to determine the structural characteristics of the emulsions: the mean particle diameter (D_{32}) and the dispersion ($D(v,0.9) - D(v,0.1)$). Particle diameter and dispersion remained constant during sample preparation and equilibration for static headspace and model mouth analysis.

A U tube viscometer (U tube VHB-320-070F; Fischer Scientific UK Ltd, Loughborough, Leicestershire, UK) was used for measuring the kinematic viscosity at 37 °C. The kinematic viscosity ($m^2\ s^{-1}$) of the emulsions was calculated from a mean measured flow time of three replicate measurements for each sample. The relative viscosity was measured by dividing the sample viscosity by the viscosity of water.

Aroma Analysis under Mouth Conditions. Aroma compounds were isolated in a model mouth system, the latest version of which has been reported by van Ruth and Roozen (*14*). Emulsion (6 mL) and artificial saliva (4 mL) were transferred into the sample flask (70 mL, 37 °C) of the model mouth system. The headspace was flushed with purified nitrogen gas (100 mL min^{-1}). The released volatile compounds were trapped in Tenax (Tenax TA 60/80; Supelco, Bellefonte, PA) for 1 min. Isolation of the volatile compounds was carried out with a plunger making up-and-down screwing movements (52 cycles min^{-1}) to simulate mastication.

The aroma compounds trapped on Tenax TA were quantified by combined gas chromatography (GC; Varian Star 3400 CX, JVA Analytical Ltd., Dublin, Ireland) and mass spectrometry (MS; Varian Saturn 3, JVA Analytical Ltd.). Desorption of the volatile compounds from Tenax was performed by a thermal desorption (220 °C, 4 min)/cold trap (−120 °C) device (Tekmar Purge and Trap 3000 concentrator, JVA Analytical Ltd.). Through a heated transfer line, the compounds were directed to the GC column (BPX5 capillary column; 60 m length, 0.32 mm i.d., and 1.0 μm film thickness; SGE, Kiln Farm Milton Keynes, UK). An initial oven temperature was 40 °C for 4 min, and the temperature was subsequently programmed to 90 °C at 2 °C min-[1], further to 130 °C at 4 °C min-[1], and finally at 8 °C min-[1] to 270 °C. Mass spectra were obtained with 70 eV electron impact ionization, while the mass spectrometer was continuously scanning from *m*/*z* 40 to 400 at a scan speed of 3 scans/s. The identities of the compounds were confirmed by comparison with spectra and retention times of single authentic compounds and bibliographic data. Six concentrations of volatile compounds in pentane were analyzed in triplicate for calibration, allowing quantification of the compounds released in the model mouth.

Aroma Analysis under Equilibrium Conditions. For equilibrium headspace gas chromatography, 0.8 mL of artificial saliva and 1.2 mL of emulsion were transferred into a 10-mL headspace vial. Three replicate vials were prepared for each emulsion. The samples were incubated at 37 °C and agitated at 750 rpm for 6 min in the automated headspace unit (Combipal-CTC Analytics system; JVA Analytical Ltd.) of the GC (Varian CP-3800; JVA Analytical Ltd.). After equilibration, 2 mL of headspace was automatically injected. The GC was equipped with an injector at 225 °C, a BPX5 capillary column (60 m length, 0.32 mm i.d., and 1.0 μm film thickness; SGE; helium carrier gas 1.9 mL min^{-1}) and a flame ionization detector at 300 °C. An initial oven temperature of −30 °C was used for 1 min, followed by a rate of 100 °C min^{-1} to 40 °C. The oven temperature was maintained at 40 °C for 4 min, and was subsequently programmed at 2 °C min^{-1} to 90 °C, further at 4 °C min^{-1} to130 °C, and finally at 8 °C min^{-1} to 270 °C.

Five concentrations of each of the compounds were analyzed in triplicate for calibration, allowing quantification of the compounds in the air phase.

Aroma Release Calculations. For quantification of aroma release, the amounts of aroma compounds released in the model mouth (*w*) were divided by the amount present in the sample flask of the model mouth before aroma isolation (*w*).

Air/Liquid Partition Coefficient Calculation. For determination of air/liquid partition coefficients of each of the compounds, air phase

Table 2. Twenty Aroma Compounds, Their Odor Descriptors, Octanol/Water Partition Coefficients (log *P*), and Densities

code	compound	odor descriptor[a]	log *P*[b]	density [g mL^{-1}]
C1	dimethyl sulfide	cabbage-like	–	0.85
C2	1-propanol	alcoholic	0.25	0.80
C3	diacetyl	buttery	0.80	0.98
C4	2-butanone	ethereal	0.29	0.80
C5	ethyl acetate	ethereal-fruity	0.73	0.90
C6	1-butanol	fusel-like	0.84	0.81
C7	2-pentanol	winey-ethereal	1.25	0.81
C8	propyl acetate	fruity	1.24	0.89
C9	3-methyl-1-butanol	fruity-winey	1.28	0.81
C10	ethyl butyrate	fruity	1.90	0.88
C11	hexanal	grassy	1.78	0.82
C12	butyl acetate	ethereal-fruity	1.82	0.88
C13	1-hexanol	chemical-winey	2.03	0.82
C14	2-heptanone	fruity-spicy	1.98	0.81
C15	heptanal	fatty-rancid	–	0.82
C16	α-pinene	pine-like	3.27	0.86
C17	2-octanone	floral	2.37	0.82
C18	octanal	fruity	2.03	0.82
C19	2-nonanol	oily	-	0.82
C20	2-decanone	citrus-like	3.77	0.82

[a] Arctander, 1994 (*16*). [b] Lide, 1997 (*17*).

concentrations (w/v) under equilibrium conditions were divided by the concentrations in the liquid phase (w/v).

Statistical Analysis. Data of triplicate aroma measurements for the various emulsions were subjected to multivariate analysis of variance (MANOVA) to determine significant differences among the samples (*15*). Principal component analysis (PCA) was conducted on the same data sets. SPSS 10.0 for Windows software was used for statistical evaluations. The extent of correlation between lipid fraction, particle diameter, and viscosity, as well as between aroma release under mouth and equilibrium conditions, was determined by Pearson's correlation coefficients. The significance level was $P < 0.05$ throughout the study.

RESULTS AND DISCUSSION

The influence of lipid fraction, emulsifier fraction, and mean particle diameter of O/W emulsions on the release of 20 aroma compounds was studied by measuring aroma release under mouth and equilibrium conditions. The compositional and structural characteristics of the seven O/W emulsions are specified in **Table 1**.

The aroma compounds examined in these aroma release experiments included alcohols (1-propanol, 1-butanol, 3-methyl-1-butanol, 2-pentanol, 1-hexanol, and2-nonanol), ketones (diacetyl, 2-butanone, 2-heptanone, 2-octanone, and 2-decanone), esters (ethyl acetate, propyl acetate, butyl acetate, and ethyl butyrate), aldehydes (hexanal, heptanal, and octanal), a terpene (α-pinene), and a sulfur compound (dimethyl sulfide). The selection of the 20 compounds was based on the physicochemical and odor properties of the compounds (**Table 2**; (*16*−*17*)). Their log *P* values, which is a measure for hydrophobicity, varied from 0.25 for the hydrophilic compounds (1-propanol) to 3.77 for the most hydrophobic compound (2-decanone). Other selection criteria were their functional group and chain length.

Effect of Emulsion Composition and Structure on Aroma Release. The relative quantities of the aroma compounds released under mouth conditions from the emulsions varying in composition and structure were measured by GC−MS and are presented in **Table 3**. The influence of lipid fraction, emulsifier fraction, and mean particle diameter on aroma release under mouth conditions was evaluated statistically for the complete data set as well as for the individual compounds by MANOVA (**Table 4**).

PCA was conducted on the aroma release data for a global interpretation of the effects of the compositional and structural factors (**Figure 1**). The first two principal components explained 88.1% of the variance in the data set. All compounds but 2-nonanol and 2-decanone showed high positive loadings on the first principal component. In general, on the second principal component, the smaller compounds had higher positive loadings and the larger compounds higher negative loadings.

Emulsion scores in the PCA map (**Figure 1**) showed that a decrease in the lipid fraction (HMH−LMH) resulted in higher positive emulsion scores on the first component and higher negative scores on the second component. The scores correlated with a general increase in aroma release, with a more pronounced increase in release of the larger, hydrophobic compounds. MANOVA of the aroma release data revealed that the lipid fraction had a significant effect on aroma release [$F(1,280) = 447.537$, $P < 0.05$]. The lipid fraction changed aroma release of 18 of the 20 aroma compounds significantly (**Table 4**), 17 of which showed an increase in release with decreased lipid fractions. The observed effect of the lipid fraction is in agreement with other studies (*4*, *18*−*19*), which demonstrated a substantial effect of the lipid content of foods on aroma release.

PCA revealed that increase of the emulsifier fraction (LLL−LML−LHL) resulted in higher negative scores of the emulsions on the second component, which correlated with a more pronounced decrease in release of the smaller, hydrophilic compounds. MANOVA demonstrated a significant effect of the emulsifier fraction on the aroma released [$F(2,280) = 52.309$, $P < 0.05$]. Increase of the emulsifier fraction decreased release of 11 of the 20 compounds significantly (**Table 4**), with most differences between the highest emulsifier concentration and the two lower emulsifier concentrations. The data agree with those of Landy et al. (*11*) and Seuvre et al. (*20*) which showed interfacial interactions between surface active agents and aroma compounds when surface active agents were present in excess.

Emulsion scores in the PCA map (**Figure 1**) demonstrate that the emulsions varying in mean particle diameter (LML−LMM−LMH and HMH−HMXH) were mainly separated along the first principal component. Increase in particle diameter correlated with a general increase in aroma release. The mean size of the particles had a significant effect on aroma release according to MANOVA results [$F(3,280) = 154.958$, $P < 0.05$]. Particle size distribution affected the release of all compounds significantly, except 2-decanone (**Table 4**). Larger sized particles coincided with increased aroma release. Charles et al. (*21*) reported a similar effect of particle diameter on the release of hydrophilic aroma compounds for salad dressings. Moreover, the data are in agreement with the theoretical models of Harrison et al. (*22*), which predicted increased aroma release with larger sized particles in O/W emulsions.

Effect of Emulsion Composition and Structure on the Thermodynamics of Aroma Release. To study the impact of the compositional and structural characteristics of the emulsions on the thermodynamic component of aroma release, the air/liquid partition coefficients of the 20 compounds in the emulsion/saliva mixture were determined for the various emulsions (**Table 5**). The various compounds had rather different partition coefficients [$F(19,280) = 3021.252$, $P < 0.05$]. The homologous series of ketones, aldehydes, and esters exhibited a clear decrease in air/liquid partition coefficients with increasing chain length. Partition coefficients of alcohols decreased as well, but to a lesser extent. They generally had lower air/liquid partition coefficients for compounds with the same number of carbons than the other groups. The lower coefficients of the

Table 3. Proportions (%) of Twenty Aroma Compounds Released from Oil-in-Water Emulsions Varying in Lipid Fraction (Φ_o), Emulsifier Fraction (Φ_e), and Mean Particle Diameter (D_{32} in μM) under Mouth Conditions (Emulsion/Saliva 60:40 ($n = 3$)

	Φ_o=0.40					Φ_o=0.65	
	Φ_e=0.007	Φ_e=0.010			Φ_e=0.014	Φ_e=0.010	
compound	D_{32} = 0.60	D_{32} = 0.60	D_{32} = 0.73	D_{32} = 0.85	D_{32} = 0.60	D_{32} = 0.85	D_{32} = 1.10
dimethyl sulfide	4.21	3.57	6.50	8.67	2.93	3.69	5.24
1-propanol	0.29	0.25	0.44	0.61	0.07	0.26	0.49
diacetyl	0.48	0.13	0.39	1.52	0.16	0.79	0.56
2-butanone	2.59	2.41	3.80	4.77	0.82	1.88	3.34
ethyl acetate	1.89	2.41	3.43	5.07	0.34	1.54	3.11
1-butanol	0.22	0.24	0.50	0.73	0.11	0.25	0.46
2-pentanol	0.28	0.32	0.53	0.84	0.15	0.31	0.42
propyl acetate	1.69	2.54	4.41	6.47	0.77	1.93	2.99
3-methyl-1-butanol	0.13	0.14	0.32	0.52	0.08	0.15	0.23
ethyl butyrate	1.08	1.62	2.74	4.05	0.27	1.28	1.76
hexanal	0.89	1.07	1.51	2.60	0.42	0.53	0.88
butyl acetate	1.14	1.20	2.32	3.49	0.46	1.01	1.41
1-hexanol	0.04	0.03	0.06	0.08	0.05	0.05	0.04
2-heptanone	0.24	0.32	0.51	0.81	0.12	0.34	0.33
heptanal	0.24	0.27	0.40	0.66	0.09	0.19	0.22
α-pinene	0.32	0.34	0.51	0.79	0.11	0.24	0.32
2-octanone	0.20	0.12	0.21	0.54	0.11	0.11	0.15
octanal	0.17	0.15	0.17	0.28	0.13	0.13	0.15
2-nonanol	2.13	1.66	2.11	1.06	0.65	1.84	3.34
2-decanone	1.43	1.23	1.70	0.71	0.70	1.51	2.33
CV[a] [%]	13.5	26.0	15.1	20.2	54.4	44.2	17.7

[a] Average coefficient of variance.

Table 4. Analysis of Variance Results: Probability Levels [%] Associated with *F*-Values of the Three Factors Lipid Fraction (Φ_o), Emulsifier Fraction (Φ_e), and Mean Particle Diameter (D_{32}) for the Release of 20 Aroma Compounds from Oil-in-Water Emulsions under Mouth Conditions and Equilibrium Conditions[a]

	mouth conditions			equilibrium conditions		
compound	Φ_o	Φ_e	D_{32}	Φ_o	Φ_e	D_{32}
dimethyl sulfide	**0.0**	16.7	**0.0**	20.9	**0.0**	**0.0**
1-propanol	**0.0**	**1.1**	**0.0**	**0.0**	**0.1**	**0.0**
diacetyl	6.3	57.2	**0.9**	**0.0**	**1.2**	**0.0**
2-butanone	**0.0**	**0.1**	**0.0**	**0.0**	**0.0**	**0.0**
ethyl acetate	**0.0**	**0.0**	**0.0**	20.3	**0.0**	**0.1**
1-butanol	**0.0**	11.8	**0.0**	**0.1**	**1.8**	**0.0**
2-pentanol	**0.0**	**2.8**	**0.0**	6.6	**0.9**	**0.0**
propyl acetate	**0.0**	10.5	**0.0**	**0.0**	**0.0**	**0.0**
3-methyl-1-butanol	**0.0**	40.2	**0.0**	23.1	**1.8**	**0.0**
ethyl butyrate	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
hexanal	**0.0**	**0.3**	**0.0**	**0.0**	**0.0**	**0.0**
butyl acetate	**0.0**	**1.2**	**0.0**	**0.0**	**0.0**	**0.0**
1-hexanol	**1.2**	37.4	**0.4**	25.4	30.7	**0.0**
2-heptanone	**0.0**	17.0	**0.2**	**2.0**	**0.0**	**0.0**
heptanal	**0.0**	**1.1**	**0.0**	**1.5**	**0.0**	**0.0**
α-pinene	**0.0**	**0.7**	**0.0**	**0.0**	**0.0**	**0.0**
2-octanone	**0.0**	20.5	**0.0**	**3.3**	**0.0**	**0.0**
octanal	**0.0**	8.8	**0.0**	23.4	**0.0**	**0.5**
2-nonanol	12.9	**1.6**	**2.4**	6.6	100.0	30.0
2-decanone	**2.8**	**1.3**	10.4	50.4	35.5	42.6

[a] In bold: significant probabilities at a 5% level.

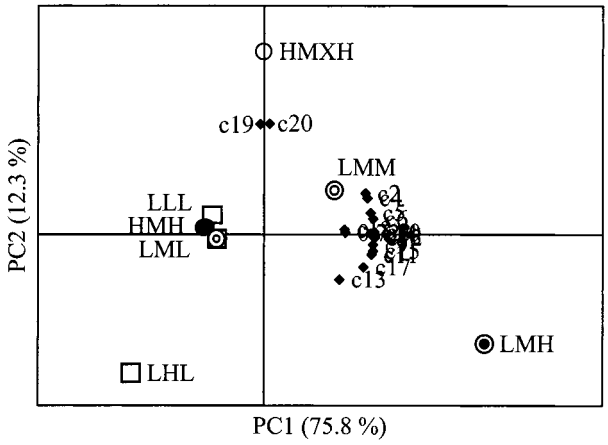

Figure 1. Scores of oil-in-water emulsions varying in lipid fraction, emulsifier fraction, and particle size distribution and loadings of 20 aroma compounds on the first and second principal component axes. Letter codes refer to samples in **Table 1**; numbers refer to compounds in **Table 2**. Symbols: ● shows the difference between low and high lipid fraction, ⊙ (concentric circles) shows the effect of particle diameter, □ shows the effect of emulsifier fraction.

alcohols are in agreement with data of Buttery et al. (*23*). Although indicated otherwise by their log *P* values (**Table 2**), present data confirm the affinity of alcohols for water in comparison with other groups of compounds shown in studies on water matrixes (*24*).

The lipid fraction did not exert an overall effect on the partitioning of the aroma compounds [$F(1,280) = 2.882$, $P < 0.05$]. The aroma compounds were at least partially soluble in both the oil and water phases (log *P* values, **Table 2**). A change in the lipid/water phase ratio caused a change in the distribution of the compounds over the continuous phase, dispersed phase, and consequently the air phase (*25*). In the present study artificial saliva had been added to the emulsions (40:60), which implies that the change in oil fraction from $\Phi_o = 0.40$ to $\Phi_o = 0.65$ altered the oil fraction in the sample in the model mouth in reality from 24% to 39%. As in previous studies a larger and significant effect of a change in oil content from 40% to 65% on aroma release from 100% emulsions was observed (*26*); it is likely that dilution of the emulsion by artificial saliva leveled out the effect of the oil fraction.

The emulsifier fraction exerted a significant effect on the air/liquid partition coefficients of the aroma compounds [$F(2,280) = 202.661$, $P < 0.05$) with generally highest air/liquid partition coefficients for the middle emulsifier concentration. However, differences were relatively small (**Table 5**). It has been shown

Table 5. Air/Liquid Partition Coefficients ($K \times 1000$) of 20 Aroma Compounds in Oil-in-Water Emulsions Varying in Lipid Fraction (Φ_o), Emulsifier Fraction (Φ_e), and Mean Particle Diameter (D_{32} in μM) with Addition of Artificial Saliva (Emulsion/Saliva 60:40 ($n = 3$)

	Φ_o=0.40					Φ_o=0.65	
	Φ_e=0.007	Φ_e=0.010			Φ_e=0.014	Φ_e=0.010	
compound	D_{32}=0.60	D_{32}=0.60	D_{32}=0.73	D_{32}=0.85	D_{32}=0.60	D_{32}=0.85	D_{32}=1.10
dimethyl sulfide	7.39	14.61	24.96	18.85	12.36	19.81	10.03
1-propanol	1.50	1.55	1.94	1.54	1.34	1.79	1.70
diacetyl	1.93	1.95	2.13	2.04	1.82	2.23	1.79
2-butanone	3.06	3.92	4.74	3.64	2.96	4.30	3.38
ethyl acetate	3.70	6.93	7.29	6.30	1.51	6.84	4.89
1-butanol	0.85	0.96	1.16	1.06	0.89	1.20	1.06
2-pentanol	1.00	1.13	1.41	1.28	1.08	1.36	1.19
propyl acetate	1.77	3.90	4.15	3.78	2.34	3.34	2.63
3-methyl-1-butanol	0.87	0.96	1.20	1.17	0.97	1.21	1.07
ethyl butyrate	1.29	2.09	2.21	2.01	1.06	1.77	1.55
hexanal	1.18	1.53	1.65	1.47	1.71	1.37	0.95
butyl acetate	1.31	1.81	1.93	1.81	1.56	1.56	1.31
1-hexanol	0.82	0.83	0.96	1.04	0.81	1.02	0.95
2-heptanone	0.62	0.87	1.04	0.89	0.52	0.81	0.67
heptanal	0.61	0.73	0.85	0.75	0.50	0.68	0.49
α-pinene	0.62	0.90	0.87	0.79	0.68	0.67	0.52
2-octanone	0.63	0.61	0.67	0.62	0.47	0.56	0.47
octanal	0.15	0.28	0.32	0.26	0.19	0.24	0.16
2-nonanol	-[a]	0.98	0.99	1.00	-	0.98	0.98
2-decanone	0.49	0.51	0.54	0.52	0.49	0.50	0.49
CV[b] [%]	4.8	6.6	14.8	3.7	4.7	3.5	4.4

[a] Below detection. [b] Average coefficient of variance.

before that surface-active agents affect equilibrium headspace concentrations of aroma compounds (*11*, *20*). As with the oil fraction, artificial saliva seems to partially extinguish the effect of the emulsifier concentration: a more pronounced effect was observed in previous studies on pure emulsions without saliva (*14*).

In comparison with the other parameters, the mean particle diameter had the largest effect on the air/liquid partition coefficients [$F(3,280) = 212.943$]. Partition coefficients of 18 out of the 20 compounds were affected. Generally, a decrease in static headspace concentration was observed for the emulsions with higher lipid fraction and larger sized particles. Particle diameter changes affect the concentration emulsifier in the interfacial region as well as the relative interface volume (volume interface/volume emulsion). As shown above, changes in the concentration emulsifier in the interfacial region exerted only a small effect. Obviously, the interface volume is of more importance, especially for the emulsions with higher oil fractions. In the studies on pure emulsions the same effect was shown (*14*). Addition of artificial saliva hardly affected this phenomenon. It is remarkable that this effect on the thermodynamics is opposite of the effect on the aroma release under mouth conditions.

Summarizing the influence of the emulsion parameters, although lipid fraction, emulsifier fraction, and mean particle diameter are of influence on air/liquid partitioning of aroma compounds in pure emulsions, saliva extinguished most of the effect of the lipid and emulsifier fractions. Despite dilution of saliva, particle size remained a factor influencing the thermodynamic component of aroma release from O/W emulsions.

The data sets of the compounds released under mouth and equilibrium conditions correlated reasonably well (Pearson correlation coefficient = 0.771), demonstrating the impact of partitioning factors on aroma release under mouth conditions. These results are in agreement with theoretical models (*22*). A correlation coefficient of 0.771 confirms the contribution of partitioning factors, but also shows that kinetic behavior of compounds has to be considered. The results agree with data of Voilley et al. (*27*) who showed that the thermodynamic and kinetic properties of aroma compounds, such as diacetyl, ethyl acetate, and ethyl butyrate vary independently of each other.

Effect of Emulsion Composition and Structure on the Kinetics of Aroma Release. The kinetic component of aroma release is represented by the mass transfer coefficient. The viscosity of emulsions is an important physical parameter affecting the mass transfer coefficient. The viscosities of the emulsions increased with increasing lipid content and with decreasing particle diameter (**Table 1**). Theoretical models predict that the mass transfer coefficient is inversely proportional to the viscosity of O/W emulsions. Moreover, the oil fraction/particle diameter ratio has been shown to be log linearly related to the viscosity (*22*). Therefore, it can be assumed that a relationship exists between the aroma release under mouth conditions and the oil fraction/particle diameter ratio. Present aroma release data of homologous series of compounds were plotted against the oil fraction/particle diameter ratios to examine this relationship (**Figure 2**). Large Pearson correlation coefficients were determined for the oil fraction/particle diameter ratios and the log aroma fraction released (0.870−0.997), confirming the relationship predicted in mathematical models. The slope values varied by 20%, which demonstrates that the effect of the oil fraction/particle diameter ratio on aroma release was rather similar for the various compounds.

Generally, a consistent decrease in aroma release was observed with increasing chain length of the compounds. The ketones, aldehydes, and esters showed similar changes: the fraction released decreased to the same extent with increasing chain length. The differences between the compounds within the groups show the differences in affinity for the emulsion, besides the differences in mass transfer. As slope values for the compounds are fairly similar, the differences between compounds within homologous series are likely to be caused by partition differences as was demonstrated in the equilibrium experiments. In contrary, the alcohols showed lower aroma release and a fairly similar curve for C3, C4, and C5, which is in agreement with results presented in previous sections. The

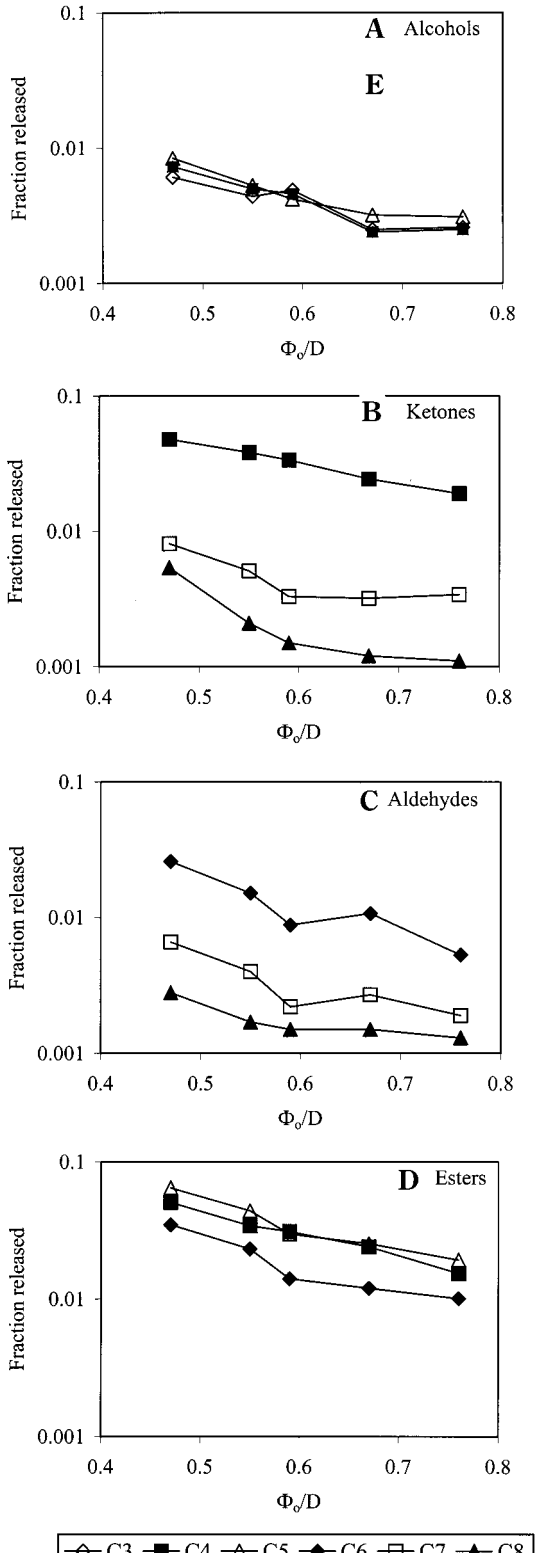

Figure 2. Aroma release as a function of the oil fraction/mean particle diameter of oil-in-water emulsions for (A) alcohols, (B) ketones, (C) aldehydes, and (D) esters. Names of aroma compounds are presented in **Table 2**.

latter indicated a smaller effect of chain length on the affinity of alcohols for oil, water, and air phase: alcohols are relatively hydrophilic.

It is remarkable that consistently higher correlation coefficients of lipid fraction/particle diameter ratio and aroma release were obtained for the smaller compounds, and lower correlation coefficients for the larger compounds, independent of the compound group. Other factors besides oil fraction and particle-size-related mass transfer factors are affecting the release of the larger sized compounds. It has been shown before that the rate-limiting step of the release of these larger compounds is the movement away from the liquid surface rather than through the liquid (*28*). Theoretically, the particle size has an effect on the diffusion of aroma compounds out of the droplets. However, for particle diameters less than about 10 μm, aroma release from droplet to continuous phase is extremely rapid ($t_{1/2} < 7 \times 10^{-5}$ s) and therefore, not likely to be the rate-limiting step in aroma release (*29*).

The concentration of emulsifier influenced mass transfer as well; differences in aroma release caused by the emulsifier fraction cannot be solely explained by thermodynamic phenomena. Generally, an increase in emulsifier fraction increased the resistance to mass transfer, which is in agreement with studies of Rogacheva et al. (*30*). The influence of emulsifier fraction on mass transfer in the continuous phase is not likely, as the viscosities of the emulsions with different emulsifier fractions were quite similar (**Table 1**).

CONCLUSIONS

The lipid fraction, emulsifier fraction, and particle size distribution of O/W emulsions showed a profound effect on aroma release. The effects observed were partially attributed to the changes in the thermodynamic component, but had a more pronounced effect on the kinetic component of aroma release.

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