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Food matrices – determination of odorant partition coefficients and application of models for their prediction

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Abstract

Foods are complex multi-component systems which are composed of volatile and non-volatile substances. The flavour profile of a food is an important criterion for the selection of our foodstuffs. The main objective of this study was the clarification of the complex relationships of the flavour release as a function of the composition of the food matrix at molecular level. Therefore the influence of matrix effects onto the odorants partition coefficients in oil–water model systems and a custard sample were investigated. The studies included a series of lactones, ester and alcohols (γ- and δ-octalactone, γ- and δ-nonalactone, γ- and δ-decalactone, ethyl hexanoate, 3-methyl-1-butanol and 2-phenylethanol). The partition coefficients were determined using static headspace gas chromatography (SH-GC). The results indicated that the custard/air partition coefficients of selected odorants are located between the water/air- and miglyol/air partition coefficients. Furthermore the mass transfer rates of selected odorants were investigated in custard- and milk powder–water samples. The values of the mass transfer rate were found higher in milk powder/water systems than in custard model. Nevertheless the results indicated that the viscosity of the matrix did not significantly influence the values of mass transfer rate of selected flavour compounds.
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Keywords: Partition coefficient; Mass transfer coefficient; Custard; Emulsion; Flavour

1. Introduction

Foods are complex multi-component systems which are composed of volatile and non-volatile substances. The flavour of a food will be characterized by odorants which were perceived by the human nose (nasal) and in the mouth–nose space, respectively. The flavour profile of a food is an important criterion for the selection of our foodstuffs. The structure of our food, in particular the presence of macromolecules as for example proteins and polysaccharides, influence the mouth feeling and the extent of the flavour release. Buck and Axel (1991) explained that the flavour sensation is caused by flavour molecules released into the vapour phase during eating and subsequently transported to the olfactory epithelium.

As Taylor et al. (2000) showed, flavour perception can be defined as: Flavour perception = aroma + taste + mouth feel + texture + pain/irritation. The authors mentioned also that's ideally, to characterise a flavour, it is necessary to measure all these parameters. As Taylor and Roberts (2004) show, there are four levels of interaction that must be taken into account when analyzing flavour: chemical interactions occurring in the food matrix, mechanical/structural interactions of the food and mastication with the release of compounds, peripheral physiological interactions, cognitive interactions among tastes, odours and somato-sensations. Interaction of the matrix components with the odorant influences its solubility and the partition coefficient. If the matrix is a mixture of two (or more) compounds, the distribution of the odorant between the two phases will depend on the quantitative composition of the matrix, which plays an important role in controlling flavour release at each step of food product separation and consumption. The chemical composition

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of a food matrix will influence perceived flavour, whether the food is primarily lipid, protein, carbohydrate or aqueous will affect release of flavour-active compounds from the matrix (Taylor & Roberts, 2004). Because many food products are emulsions of lipids and water, such as milk and milk products, the lipid content is an important variable in the food matrix. Removal or reduction of lipids can lead to an imbalanced flavour, often with a much higher intensity than the original full fat food (Ingham, Taylor, Chevance, & Farmer, 1996; Widder & Fischer, 1996). Flavour compounds solved in oil showed lower headspace concentrations compared to odorants solved in water (Buttery et al., 1971, 1973). This effect was confirmed by mathematical models (Harrison et al., 1997), headspace analysis (Schirle-Keller et al., 1994) and sensory analysis (Ebeler et al., 1988; Guyot et al., 1996). Extensive reviews of the effects of lipids on the rate and amount of aroma released have been published (De Roos, 1997; Hatchwell, 1994; Plug & Haring, 1993). De Roos (1997) reported that in products containing aqueous and lipid phases, a flavour compound is distributed over three phases: fat (or oil), water and air. Flavour release depends on oil content, which affects the partition of aroma compounds during the different emulsion phases (lipid, aqueous, and vapour). Flavour release from the oil/fat phase of a food proceeded at a lower rate than from the aqueous phase. This was attributed, first to the higher resistance to mass transfer in fat and oil than in water and, second to the fact that in oil/water emulsions flavour compounds had initially to be released from the fat into the aqueous phase before they could be released from the aqueous phase to the headspace. In the case of emulsions the structure itself has been shown to affect the release rate of flavour (Overbosch et al., 1991; Salvador et al., 1994). The effects of the primary structural and compositional properties of emulsions on the release of aroma have been both systematically investigated (Miettinen et al., 2002; Van Ruth et al., 2002). Van Ruth et al. (2002) examined the influence of compositional and structural properties of oil-in-water emulsions on aroma release under mouth and equilibrium conditions. The results obtained, showed that the decrease in lipid fraction and emulsifier fraction, as well as increase in particle diameter, increased aroma release under mouth conditions. Miettinen et al. (2002) investigated the effects of oil-in-water emulsion structure and composition of the matrix on the release of linalool and diacetyl. The results indicated that the lipid content strongly affected the release of linalool, but it was not as critical a factor in the release of the more polar compound diacetyl. Flavour release depends on the ability of the aroma compounds to be in the vapour phase and therefore on their affinity for the product, which participates in their rate of transfer (Voilley, Espinosa-Diaz, Druaux, & Landy, 2000). Kinsella (1989) reported that several mechanisms might be involved in the interaction of odorants with food components and therefore responsible for the release of volatile components from food: diffusion phenomena influenced by the viscosity and specific and non-specific binding of aroma compounds to macromolecules influence the intermolecular interactions.

The present studies are part of a research project (COST Action 921) at EU level. The objectives of the research work are the clarification of the complex relationships of the odorant partition coefficients as a function of the composition of the food. Different approaches published in the literature were used for the prediction of odorant partition coefficients (Log*P*) and compared with experimental values.

2. Experimental part

2.1. Materials and methods

2.1.1. Reference compounds

2-Phenylethanol, 3-methyl-1-butanol, ethyl hexanoate, γ- and δ-decalactone, γ- and δ-nonalactone and γ-octalactone were purchased from Sigma–Aldrich (Steinheim, Germany). δ-Octalactone and ethyl octanoate was obtained from Lancaster (Eastgate, White Lund, Morecambe, England). The purities of reference compounds (GC analysis) were equal or higher than 98%. The strawberry flavour composition was a gift of Givaudan (Dubendorf, Switzerland). The composition was as follows: furaneol 5 (mg/g), vanillin 5 (mg/g), methyl cinnamate (24 mg/g), ethyl hexanoate (20 mg/g), ethyl butanoate (90 mg/g), benzyl acetate (2 mg/g), styrallyl acetate (1 mg/g), γ-decalactone (20 mg/g), methyl anthranilate (1 mg/g), ethyl iso-pentanoate (10 mg/g), hexanal (1 mg/g), (*Z*)-3-hexenyl acetate (5 mg/g), (*Z*)-3-hexenol (15 mg/g), methyl dihydrojasmonate (5 mg/g), β-ionone (1 mg/g) and triacetin (795 mg/g).

Miglyol 812 (fractionated coconut oil composed of caprylic acid (50–65%) and capric acid (30–45%) triglycerides) was a gift of Sasol GmbH (Witten, Germany). Emulsifier Tween 85 (polyoxyethylene sorbitan trioleate) (HLB (hydrophilic–lipophilic-balance) value: 11.0 ± 1.0) was obtained from Sigma–Aldrich (Steinheim, Germany). Modified Tapioca starch E 1442 (Cerestar C*Creamtex 75720) and κ-carrageenan (Meypro™ Lact HMF, Gelymar Lot 114) were a gift of the ETH Zürich (Institute of Food Science and Nutrition, Zürich, Switzerland) Full fat milk powder (26% fat in the dry matter) from Friesland Coberco Dairy Foods (Corporate Research, Deventer, Netherland) and saccharose from Sigma–Aldrich (Steinheim, Germany).

2.1.2. Model custard preparation

The chemical composition of the custard (g/100 g custard) was as follows: 4 g modified tapioca starch E 1442 (Cerestar C* Creamtex 75720), 5 g saccharose, 0.01 g κ-carrageenan, 0.06 g Givaudan flavour (strawberry aroma), 90 g rehydrated full fat milk powder (3.5% fat), water (weight to yield a total of 100 g). Preparation procedure (200 g custard sample): Full fat milk powder (26% fat; 23.5 g) was mixed with water (45 °C; 156.5 g) and stored for 24 h in the refrigerator. κ-carrageenan (0.02 g), saccharose (10 g) and starch (8 g) were mixed in a flask and rehydrated milk powder was added at room temperature

(25 °C). The mixture was placed in a water bath at 97 ± 0.5 °C and stirred constantly at 150 rpm. The water bath temperature was controlled using a thermostat and the product temperature was measured. After 15 min the product temperature reached 94 ± 1 °C and heating was continued at this temperature for 15 min. After the heating process the evaporated water was replaced gravimetrically to 200 g. The odorants (0.12 g Givaudan flavour, 200 mg 3-methyl-1-butanol and 200 mg 2-phenylethanol) was added to the mixture and the hot custard was stirred and cooled to 25 °C in ice water within 15 min. Before analysis the custard was stored two days in a refrigerator at 8 °C. Furthermore the following six 'model custard mixtures' were prepared by the same procedure as described above for the 'original custard' (sample 4) by leaving out selected ingredients from the recipe and by replacement of modified starch with native starch: sample 1 (rehydrated milk powder and water), sample 2 (modified tapioca starch and water), sample 3 (native tapioca starch and water), sample 5 (modified tapioca starch, saccharose and water), sample 6 (κ-carrageenan, rehydrated milk powder, native tapioca starch, saccharose and water) and sample 7 (κ-carrageenan, modified tapioca starch, saccharose and water). The prepared custard sample has a density of 1.07 g/cm^3.

2.1.3. Model mixtures

Model mixtures: Water (tap water), Miglyol type 812 and three emulsions with the following chemical composition: deionised water, miglyol and emulsifier Tween 85 (emulsion I: 47.5 + 47.5 + 5 (w/w/w), emulsion II: 85.5 + 9.5 + 5 (w/w/w) and emulsion III: 90.25 + 4.75 + 5 (w/w/w)). For the preparation of the emulsions an IKA Ultra-Turrax homogenizer (Typ T 18/10, 18 mm shaft tube diameter, 12.7 mm rotor diameter, Janke & Kunkel, Germany) and an ultrasound–disintegrator (Branson sonifier, B-15, Henemann, Schwäbisch Gmünd, Germany) were used. The emulsions (100 g) were prepared in glasses by mixing water, the emulsifier Tween 85 (polyoxyethylene sorbitan trioleate) and a known quantity of odorant solved in miglyol (20 mg – 2000 mg/100 g emulsion) with deionised water by an Ultra Turrax homogenizer for 3 min at rotation speed indicator 4 (scale: 1–10). After that miglyol type 812 was added slowly during mixing. Afterwards an ultrasound-disintegrator was used in the continuous modus for 4 min (control 7, scale: 1–10) for obtaining a stable emulsion. To obtain a stable emulsion a cell-disruptor disintegrator was used for further homogenizing. The emulsions were stored at room temperature for 1 h to stabilize and 10 ml of the emulsion was put in vials (250 ml) for equilibration (1 h, 30 °C). The samples were analyzed by static headspace analysis (SHA).

2.1.4. Static headspace analysis (SHA) of model mixtures

Model mixtures were analyzed by static headspace analysis (SHA) at a Chrompack CP 4010 gas chromatograph connected to the TCT/PTI 4001 (Varian-Chrompack, Darmstadt; Germany) headspace injector operating in the TCT thermal desorption mode. Model mixtures were put into a thermostated vessel (volumes: 20 and 250 ml, 30 °C), sealed with a septum and equilibrated for 3 h. Headspace gas was drawn by a gas tight syringe (volumes: 1 ml and 5 ml; SGE, Germany) and injected into the TCT system (velocity of injection: 10 ml/min). The syringes were equipped with a valve, which is closed after transferring the headspace sample into the syringe, to prevent the losses of the volatile compound. The TCT/PTI 4001 system operated in the desorption mode for 15 min at a temperature of 200 °C and a desorption flow rate of 20 ml helium. The fused silica trap (30 cm × 0.53 mm, coated with CP-Sil5CB, 5 μm film thickness, Varian-Chrompack, Darmstadt, Germany) was cooled with liquid nitrogen at −110 °C and after 15 min the trap was heated up to 200 °C and the temperature was held for 1 min. The trapped compounds were flushed by the helium flow into the GC (Hewlett-Packard 5890 Series II, Agilent, Waldbronn, Germany) onto the capillary DB-FFAP (J&W Scientific). The GC oven temperature was held for 1 min at 35 °C and then the temperature was raised at 40 °C/min to 60 °C, held for 1 min, then raised at 8 °C/min to 240 °C, and held for 20 min isothermally. The compounds were analysed by GC-FID (flame ionization detector). Quantification of the odorants in the headspace was achieved by an external calibration by injection of standard compounds solved in pentane (1 μL, concentration range: 2–200 ng/μL) direct after the application of the headspace gas of the sample. The FID response and the recorded peak areas were linear in the above mentioned concentration range. The headspace odorant concentration was determined by comparison of the area of headspace sample to the area obtained by injecting of the standard solution. Adsorptions of the odorants at the gastight syringe were checked by the method reported by Guth and Sies (2001).

2.1.5. Static headspace analysis (SHA) of custard samples

For the determination of the headspace concentration of selected aroma compounds in custard samples (5 g, custard density 1.07 g/cm^3) the GC CP-3380 (Varian-Chrompack, Darmstadt, Deutschland) in combination with the Combi-Pal static headspace auto-sampler (CTC Analytics AG, Zwingen, Switzerland) was used. The following general conditions were applied: splitless injection mode (0.5 ml headspace gas), FID detector, HP-1 capillary (30 m × 0.53 mm, 2.65 μm film thickness, Hewlett-Packard, Germany) and ZB-FFAP capillary (30 m × 0.32 mm, 0.5 μm film thickness, Phenomenex, Aschaffenburg, Germany), gas tight syringe (volume 1 ml), headspace vials (volume 20 ml, 75.5 × 22.5 mm, Sigma–Aldrich, Steinheim,Germany). Quantification of the odorants in the headspace was achieved by an external calibration as described above for the TCT/PTI 4001 headspace system.

2.1.6. Determination of odorant concentration in custard samples

For the determination of the losses of odorants during custard preparation and storage the concentrations of

selected compounds were investigated by the standard addition method after custard preparation and storage. The custard (5 g) was stocked with a known quantity of corresponding odorant (0%, 10%, 20% and 30% of the original concentration added during custard preparation). The odorant concentration in the custard sample was investigated by SHA as described above. The peak areas of the four samples were plotted against the concentrations added. The amount of the odorant in the custard was calculated from the corresponding regression line obtained from the four values.

3. Results and discussion

3.1. Partition coefficients of selected odorants in model systems (water, miglyol and emulsions)

The partition coefficients of ethyl hexanoate, 3-methyl-1-butanol, 2-phenylethanol and various lactones (γ- and δ-decalactone, γ- and δ-nonalactone and γ- and δ-octalactone) were determined by static headspace analysis (SHA) and gas chromatography (GC) in model systems (water, miglyol and emulsions). The adsorption effects of the odorants to the gas-tight syringe were checked by the method reported in the literature (Guth & Sies, 2001) and were taken into account by the calculations of the odorant headspace concentrations. The procedure was as follows (Guth & Sies, 2001): After headspace sampling (syringe 1, volume 5 ml) a second gas-tight syringe (volume 5 ml) was coupled to syringe 1 and a defined gas volume of syringe 1 was transferred to syringe 2. Injection of a defined gas volume of syringe 2 followed by a direct injection of an identical gas volume of syringe 1 into the TCT-GC system. The peak area (FID) of the odorant were recorded for both injections (syringes 1 and 2, respectively) and the area difference (syringes 1 and 2) calculated. From the area difference the odorant adsorption to the gas tight syringe can be estimated.

Furthermore the influence of the model systems (e.g. water content of model mixture) on the adsorption values was investigated. Adsorptions are summarized in Table 1 and calculated from five replicates (standard deviation: ±15%). Table 1 shows that the adsorption values of odorants at the gas tight syringe range from 11% to 89%, depending on compound and model system. The highest adsorption values were found for δ-decalactone above water and emulsions model mixtures (83–89%). The results indicate that the odorant adsorption to the gas-tight syringe, depends on the polarity of the odorant and the model composition.

The partition coefficients ($\mathrm{Log}P_{\mathrm{Water/Air}}$ and $\mathrm{Log}P_{\mathrm{Miglyol/Air}}$) of selected odorants were determined by SHA and summarized in Table 2. The adsorption effects of odorants at the gas-tight syringe (cf. Table 1) were took into account by the calculation. Table 2 indicates that in the series of δ- and γ-lactones the $\mathrm{Log}P_{\mathrm{Water/Air}}$ decreased with increasing lipophilicity and carbon number of the odorant, respectively. The miglyol/air partition coefficients ($\mathrm{Log}P_{\mathrm{Miglyol/Air}}$) of the series of γ- and δ-lactones are increasing with increasing lipophilicity of the odorant. The $\mathrm{Log}P_{\mathrm{Miglyol/Air}}$ of δ-lactones are higher than for the γ-lactones with the same carbon number. The differences of the water/air- and miglyol/air partition coefficients (ΔLog$P$: $\mathrm{Log}P_{\mathrm{Miglyol/Air}}$–$\mathrm{Log}P_{\mathrm{Water/Air}}$) are included in Table 2. For ethyl hexanoate the concentration in the headspace above water is higher than in the headspace above miglyol by a factor of 100. In contrast to ethyl hexanoate, the concentration of 2-phenylethanol in the headspace above water compared to the headspace concentration above miglyol is higher only by factor of 5. From Table 2 it is obvious that the ΔLog$P$ depends on the lipophilicity of the odorant. Increasing lipophilicity of an odorant leads to higher ΔLog$P$ values as shown for the series of γ- and δ-lactones (e.g. ΔLog$P$ of γ-decalactone = 2.7 and ΔLog$P$ of γ-octalactone = 1.4).

Table 1
Adsorption of selected flavour compounds at the gas-tight syringe depending on the model system

Compound	Adsorption (%)[a]				
	Water	Miglyol	Emulsions		
			I[b]	II[c]	III[d]
Ethyl hexanoate	59	56	55	60	50
3-Methyl-1-butanol	63	55	58	47	58
2-Phenylethanol	23	55	48	56	36
γ-Octalactone	5	24	23	30	48
γ-Nonalactone	34	26	23	28	30
γ-Decalactone	19	46	68	77	58
δ-Octalactone	18	18	18	22	47
δ-Nonalactone	67	30	11	38	61
δ-Decalactone	83	39	87	89	85

[a] Three to five replicates/sample, standard deviation: ±15%.
[b] Emulsion I: water/miglyol/emulsifier Tween 85: (47.5 + 47.5 + 5, w/w/w).
[c] Emulsion II: water/miglyol/emulsifier Tween 85: (85.5 + 9.5 + 5, w/w/w).
[d] Emulsion III: water/miglyol/emulsifier Tween 85: (90.25 + 4.75 + 5, w/w/w).

The prediction of air/vegetable oil partition coefficients of a number of flavour compounds (aldehydes, ketones and alcohols) was reported by Buttery et al. (1973). The authors proposed an equation which can be re-written for the determination of the miglyol/air partition coefficients as follows:

$$P_{\mathrm{Miglyol/Air}} = \frac{1}{p_0 \times \gamma \times (\text{solvent conversion factor})}$$

p_0 (vapour pressure of compound), γ is the activity coefficient (generally approaches 1) and solvent conversion factor proposed for vegetable oils: 5.2×10^{-5}.

The vapour pressures of odorants and the experimentally determined miglyol/air partition coefficient together with estimated values (according to the equation of Buttery et al. (1973)) are summarized in Table 2. The vapour pressures of the odorants were determined by SHA-GC of the pure compounds. Table 2 shows that the experimentally

Table 2
Partition coefficients ($\mathrm{Log}P_{\mathrm{Water/Air}}$ and $\mathrm{Log}P_{\mathrm{Miglyol/Air}}$) of selected odorants in miglyol and water

Compound	Vapour pressure[a,b] (Pa, 30 °C)	$\mathrm{Log}P_{\mathrm{Water/Air}}$[a,b] (30 °C)	$\mathrm{Log}P_{\mathrm{Miglyol/Air}}$[a,b] (30 °C)	$\mathrm{Log}P_{\mathrm{Miglyol/Air}}$ predicted[c]	$\Delta\mathrm{Log}P$ ($\mathrm{Log}P_{\mathrm{Miglyol/Air}} - \mathrm{Log}P_{\mathrm{Water/Air}}$)
Ethyl hexanoate	165	2.2	4.3	4.2	2.1
2-Phenylethanol	13	5.2	5.7	5.3	0.5
3-Methyl-1-butanol	582	2.5	3.3	3.6	0.8
γ -Octalactone	7.0	4.8	6.2	5.6	1.4
γ-Nonalactone	1.1	4.2	6.3	6.4	2.1
γ-Decalactone	0.9	3.9	6.6	6.5	2.7
δ-Octalactone	2.4	5.7	6.2	6.0	0.5
δ-Nonalactone	0.8	5.2	6.5	6.5	1.3
δ-Decalactone	0.5	4.6	6.9	6.7	2.3

[a] Three to five replicates/sample, standard deviation: ±15%. The ratio was calculated by mass values of odorant in sample and in headspace above sample.
[b] Adsorptions of pure compounds at the gas-tight syringe were taken into account (cf. Table 1).
[c] Predicted $\mathrm{Log}P_{\mathrm{Miglyol/Air}}$ values were calculated according to the equation published by Buttery et al. (1973). The activity coefficient (γ) was assumed to be 1.

determined $\mathrm{Log}P_{\mathrm{Miglyol/Air}}$ values are quite close to the estimated values.

The following three emulsion models were prepared with different water and miglyol amounts: emulsion I (water/miglyol/Tween 85, 47.5 + 47.5 + 5, w/w/w), emulsion II (water/miglyol/Tween 85, 85.5 + 9.5 + 5, w/w/w) and emulsion III (water/miglyol/Tween 85, 90.25 + 4.75 + 5, w/w/w). Emulsion I–III were from type oil in water (O/W) (e.g. emulsion I: average particle size 4.2 μm^2, particle diameter 2.3 μm, data not shown). The partition coefficients ($\mathrm{Log}P_{\mathrm{Emulsion/Air}}$) of the three emulsions (I–III) were determined for selected odorants and the values are summarized in Table 3. In the series of γ-lactones the headspace concentrations above emulsions I–III decrease slightly with increasing carbon number of the compound. Increasing the amount of lipid (miglyol) in the emulsion resulted in an increase of the $\mathrm{Log}P_{\mathrm{Emulsion/Air}}$ value and therefore decreased the headspace concentration of the corresponding odorant. For instance, in the series of γ-lactones a reduction of the miglyol content from 47.5 (emulsion I) to 4.75% (emulsion III) leads to an increase of the odorant headspace concentration by a factor of about 3–4 ($\Delta\mathrm{Log}P = 0.5$–$0.6$). The aforementioned effect is more pronounced with the compound ethyl hexanoate with a factor of 8 and less distinct with 2-phenylethanol with a factor of 2.

A prediction of odorant partition coefficients in emulsions with different lipid content was proposed by Buttery et al. (1973) according to the following equation:

$$P_{\mathrm{Emulsion/Air}} = F_{\mathrm{Water}} \times P_{\mathrm{Water}} + F_{\mathrm{Oil}} \times P_{\mathrm{Oil}}$$

P_{Water} is the water/air partition coefficient, P_{Oil} is the oil/air partition coefficient, and F_{Water} is the fraction of water in the mixture, F_{Oil} is the fraction of oil in the mixture. The total volume, $F_{\mathrm{Water}} + F_{\mathrm{Oil}}$ is equal to 1.

Using the above mentioned equation, it is possible to predict miglyol-water/air partition coefficients for emulsions I–III. The results obtained are presented in Table 3 together with the experimental values. Table 3 indicates that the predicted values of emulsion I (highest lipid content) show good correlation with the experimental values. The quality of the prediction of the partition coefficients decrease with increasing water contents in the models (emulsions II and III).

Table 3
Partition coefficients ($\mathrm{Log}P_{\mathrm{Emulsion\ (I–III)/Air}}$) of selected aroma compounds in emulsion model systems and predicted values

Compound	$\mathrm{Log}P_{\mathrm{Emulsion\ I/Air}}$ (30 °C)[a,b]		$\mathrm{Log}P_{\mathrm{Emulsion\ II/Air}}$ (30 °C)[a,b]		$\mathrm{Log}P_{\mathrm{Emulsion\ III/Air}}$ (30 °C)[a,b]	
	Experimental	Predicted[c]	Experimental	Predicted[c]	Experimental	Predicted[c]
Ethyl hexanoate	4.2	4.0	3.4	3.3	3.3	3.1
2-Phenylethanol	5.7	5.6	5.5	5.3	5.4	5.3
3-Methyl-1-butanol	3.6	3.1	3.4	2.7	3.2	2.7
γ-Octalactone	6.0	5.9	5.8	5.3	5.5	5.1
γ-Nonalactone	6.3	6.0	5.9	5.3	5.9	5.1
γ-Decalactone	6.5	6.3	6.0	5.6	5.9	5.3
δ-Octalactone	6.3	6.1	6.1	5.8	5.8	5.7
δ-Decalactone	6.6	6.6	5.9	5.9	6.0	5.6

[a] Emulsion I: water/miglyol/Tween 85 (47.5 + 47.5 + 5, w/w/w), emulsion II: water/miglyol/Tween 85 (85.5 + 9.5 + 5, w/w/w) and emulsion III: water/miglyol/Tween 85 (90.25 + 4.75 + 5, w/w/w). Three to five replicates/sample, standard deviation: ±15%.
[b] Adsorptions of odorants at the gas-tight syringe were taken into account (cf. Table 4).
[c] According to Buttery et al. (1973).

3.2. Static headspace analysis (SHA) of custard samples

The knowledge about the binding behaviour of an odorant to a macromolecule in relation to their partition coefficients, which is defined as ratio of the odorant concentration in the food matrix to the concentration in the headspace above the food, is of importance for the production of high-quality foodstuffs. The main goal of the following subject was first, the investigation of the flavour release as a function of matrix components and second, the time influence on the flavour release (mass transfer coefficients of odorants). As outlined in Section 2, the 'original' custard (sample 4) was made of the following ingredients: water, saccharose, rehydrated milk powder, modified tapioca starch, κ-carrageenan, Givaudan flavour (for ethyl hexanoate) and selected odorants (3-methyl-1-butanol, ethyl octanoate and 2-phenylethanol) solved in triacetin. The determination of the losses of odorants during the production and storage of the custard samples were made by quantification of odorants after custard preparation. The results are summarized in Table 4. The recoveries of selected odorants ranged from 59% to 93%. The highest partition coefficient was found for 2-phenylethanol ($\mathrm{Log}P_{\mathrm{Custard/Air}} = 5.2$) followed by ethyl octanoate ($\mathrm{Log}P_{\mathrm{Custard/Air}} = 4.1$).

Table 4
Partition coefficients ($\mathrm{LogP_{Custard/Air}}$) and recoveries of selected odorants in the prepared custard sample

Aroma compounds	μg odorant/g custard recipe	μg odorant/g custard prepared	Recovery (%)[a]	$\mathrm{Log}P_{\mathrm{Custard/Air}}$[a]
Ethyl hexanoate	120	112	93	3.3
2-Phenylethanol	1023	827	81	5.2
Ethyl octanoate	878	520	59	4.1
3-Methyl-1-butanol	809	575	71	3.3

[a] Two replicates/sample, standard deviation: ±10%.

In further studies the influence of the matrix components (κ-carrageenan, modified- and native tapioca starch and milk powder) on the headspace concentrations of odorants were investigated. For this purpose, seven model mixtures (samples 1–7, cf. Section 2) containing one or more of the above mentioned matrix components were prepared.

For 3-methyl-1-butanol (Fig. 1) the lowest concentration in the headspace was found in the model mixture containing only modified tapioca starch and water (sample 2, 222 ng/ml). The headspace concentration of 3-methyl-1-butanol above sample 3 (Fig. 1) which contains native tapioca starch instead of modified starch was 247 ng/ml. This means that native and modified tapioca starch have similar effect on the flavour release. The highest concentration in the headspace was found in the model mixture containing milk powder and water (sample 1, 390 ng/ml). Recapitulating the facts for 3-methyl-1-butanol the conclusion is that the matrix components have only slight effects on the headspace concentrations.

In contrast to 3-methyl-1-butanol, ethyl hexanoate shows a more distinct effect on the matrix composition (Fig. 2). The highest headspace concentration of ethyl hexanoate was found above sample 2 containing only water and modified tapioca starch (605 ng/ml air). The lowest headspace concentration of the odorant was measured above the 'original' custard (sample 4, 58 ng/ml air). The headspace concentration of ethyl hexanoate increased slightly (70 ng/ml air) in sample 5 which was prepared without κ-carrageenan compared to the 'original' custard. The sample without milk powder (sample 7) shows a drastic effect on the headspace concentration of ethyl hexanoate compared to the 'original' custard. The concentration was by a factor of eight higher (457 ng/ml air) compared to the original custard (58 ng/ml

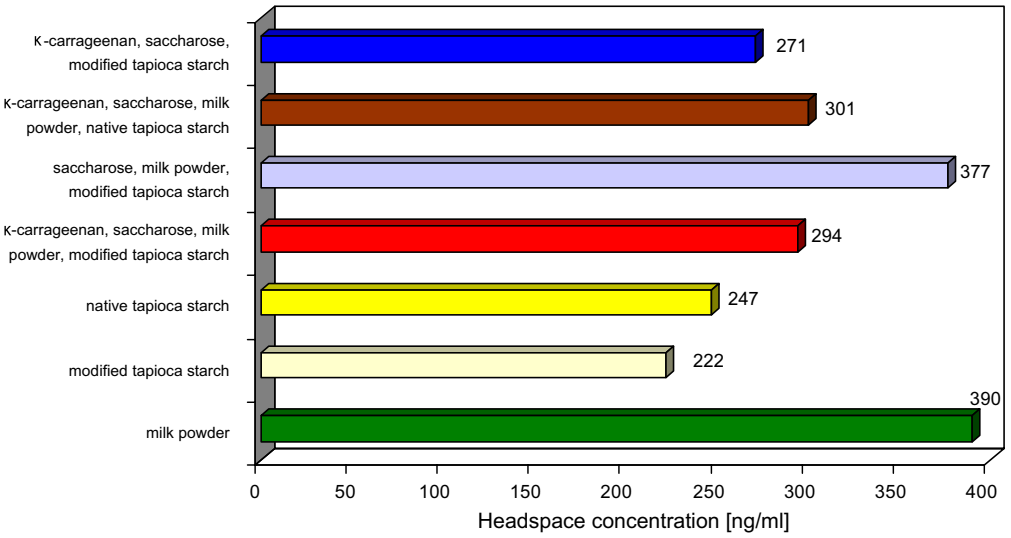

Fig. 1. Headspace concentrations of 3-methyl-1-butanol above "original" and modified custard samples. Two replicates/sample, standard deviation: ±10%.

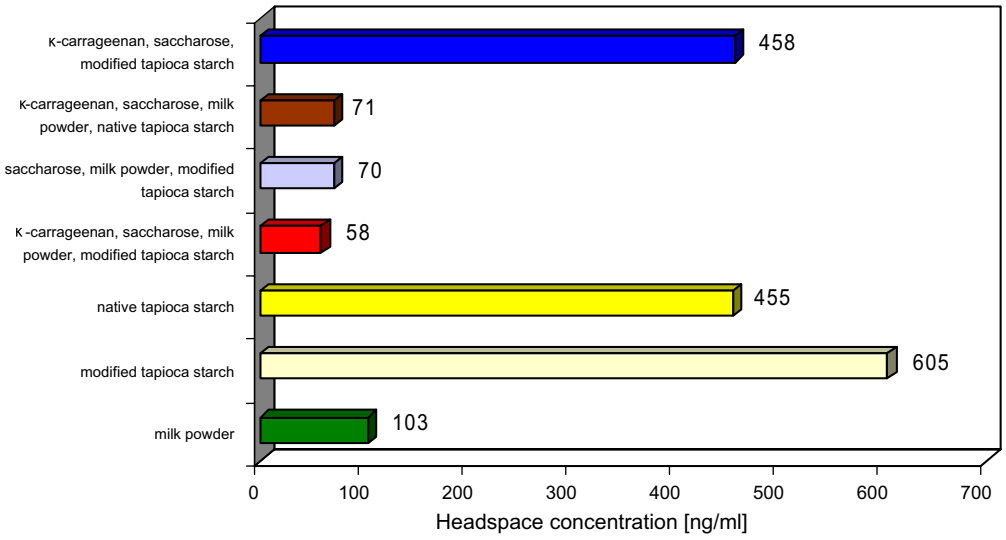

Fig. 2. Headspace concentrations of ethyl hexanoate above "original" and modified custard samples. Two replicates/sample, standard deviation: ±10%.

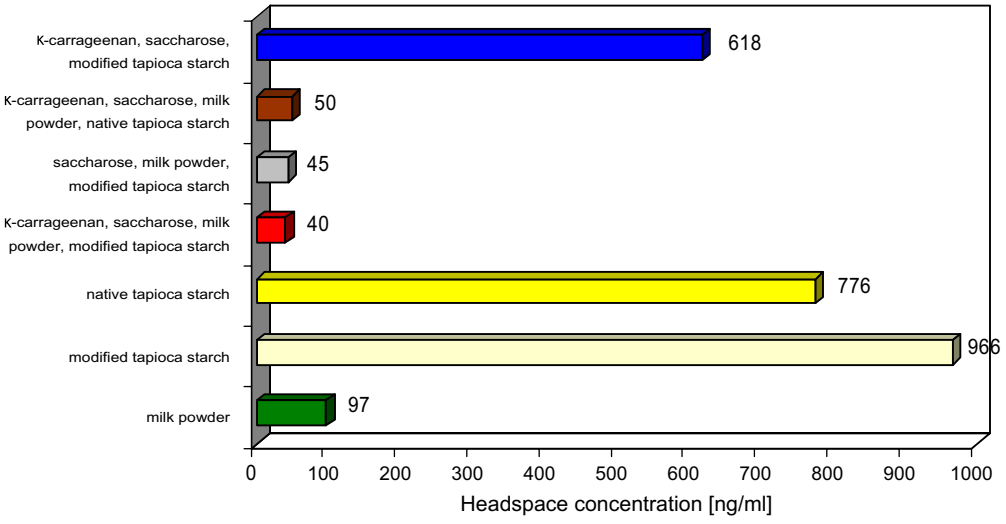

Fig. 3. Headspace concentrations of ethyl octanoate above "original" and modified custard samples. Two replicates/sample, standard deviation: ±10%.

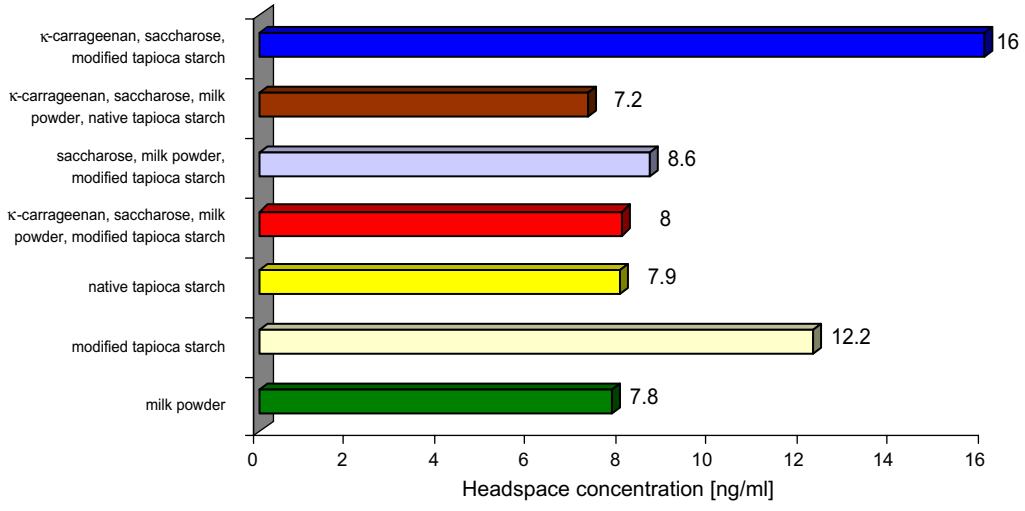

Fig. 4. Headspace concentrations of 2-phenylethanol above "original" and modified custard samples. Two replicates/sample, standard deviation: ±10%.

air). Similar effects were observed for ethyl octanoate (Fig. 3). The results indicate that in particular the constituents of the milk (proteins and lipids) are responsible for the reduction of ethyl hexanoate and ethyl octanoate in the headspace above the 'original' custard. Caused by these changes the consumer's acceptance can go back for a food or be promoted. The strength of the interaction of an odorant with a macromolecule should be considered closer for the proteins and lipids present in milk.

The highest headspace concentration of 2-phenylethanol (Fig. 4) was found in the modified sample where no milk powder was present (sample 7, 16 ng/ml), and the lowest concentration in the modified sample where modified tapioca starch was replaced by native tapioca starch (sample 6, 7.2 ng/ml). A comparison of the 2-phenylethanol headspace concentrations in the 'original' custard (sample 4) and the modified custards (samples 1–3 and samples 5–7) shows that the observed headspace concentrations varies only from 7.8 ng/ml to 16 ng/ml air.

A comparison of the partition coefficients of the model system emulsions III (containing 4.75% lipid) with that of the 'original custard' reveal that for the odorants ethyl hexanoate ($\mathrm{Log}P_{\mathrm{Custard/Air}} = 3.3$, $\mathrm{Log}P_{\mathrm{EmulsionIII/Air}} = 3.3$; Tables 2 and 3), 2-phenylethanol ($\mathrm{Log}P_{\mathrm{Custard/Air}} = 5.2$, $\mathrm{Log}P_{\mathrm{EmulsionIII/Air}} = 5.4$; Tables 2 and 3) and 3-methyl-1-butanol ($\mathrm{Log}P_{\mathrm{Custard/Air}} = 3.3$, $\mathrm{Log}P_{\mathrm{EmulsionIII/Air}} = 3.2$; Tables 2 and 3) the Log$P$ values are close together. This fact allows the conclusion that the lipid present in the custard is mainly responsible for flavour release.

3.3. Determination of mass transfer coefficients of some flavour compounds studied, in custard- and rehydrated milk powder samples

The mass transfer of flavour compounds between two phases is the main mechanism of flavour release (Marin, Baek, & Taylor, 2000). The mass transfer coefficients between the liquid phase (custard and rehydrated milk powder) and the headspace were studied for selected odorants. The mass transfer coefficients were calculated using software package TableCurve2D (SPSS, Erkrath, Germany). The time influence to the flavour release was analysed by SHA-GC and the data is shown in Fig. 5, for e.g., ethyl octanoate. The data points (5–10 values/sample) from the graphics were fitted according to the following equation:

$$\int_0^{c_g} \frac{\mathrm{d}c_g}{K \cdot c_l - c_g} = \int_0^t \frac{k \cdot A}{V_R} \cdot \mathrm{d}t$$

$$c_g(t) = K \cdot c_{l(t=0)} \cdot (1 - \mathrm{e}^{\frac{-k \cdot A}{V_R} \cdot t})$$

K (partition coefficient = odorant concentration headspace/odorant concentration sample), k (mass transfer coefficient (m/s)), A (surface area of sample, m^2), V_R (Volume of whole gas compartment above sample, m^3), c_g (odorant concentration in the headspace, ngIml air), c_l (odorant concentration liquid ng/ml sample).

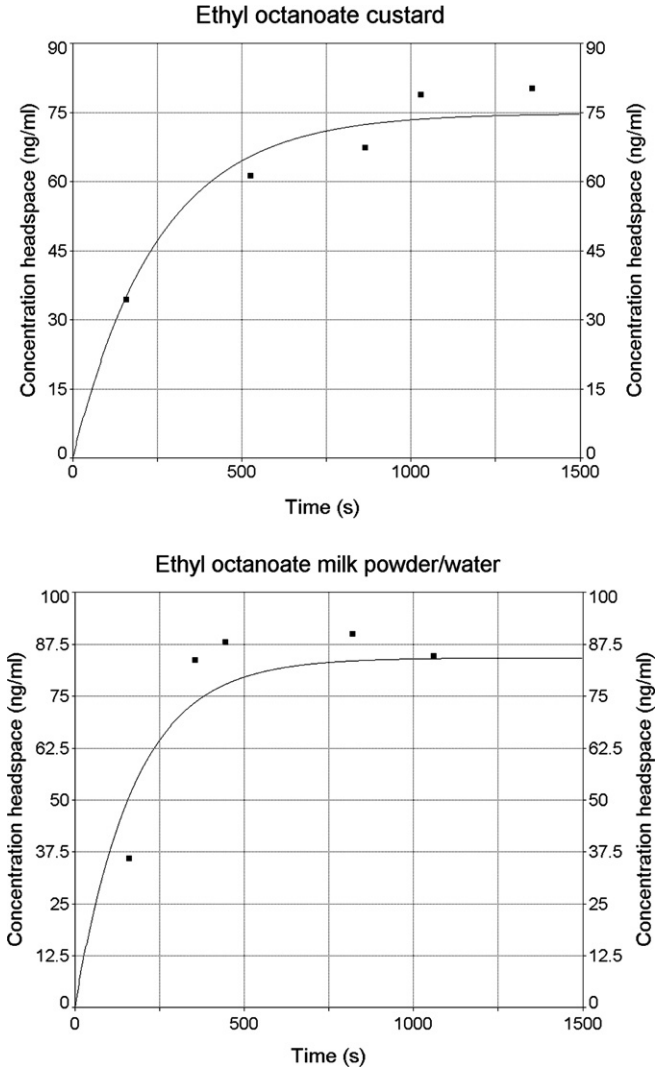

Fig. 5. Time influence onto the headspace concentration of ethyl octanoate in custard and rehydrated milk powder.

Table 5
Calculated mass transfer coefficients (k) of odorants in the 'original custard' and in rehydrated milk powder

Model systems	Mass transfer coefficients (m/s)[a]	
	Original custard	Rehydrated milk powder
2-Phenylethanol	2.2×10^{-4}	2.4×10^{-4}
3-Methyl-1-butanol	2.6×10^{-4}	1.8×10^{-4}
Ethyl hexanoate	1.9×10^{-4}	2.0×10^{-4}
Ethyl octanoate	1.7×10^{-4}	2.5×10^{-4}

[a] Mass transfer coefficients were calculated according to equation mentioned in Section 3 from the odorant time/headspace-concentration curves (e.g. Fig. 5). The following parameters were used for curve fitting: K (partition coefficient of odorant Table 4, $K = 1/10^{\mathrm{Log}P}$), c_l (odorant concentration in the matrix of custard and rehydrated milk powder after preparation, ng/ml Table 4), A (area of matrix/headspace interface, 3.3×10^{-4} m^2), V_R (volume of whole gas compartment, 15.3×10^{-6} m^3). Standard deviation ±20% (curve fitting, experimental values).

From the above mentioned equation the mass transfer coefficients (k) of selected odorants in the 'original' custard

(sample 4) and rehydrated milk powder model (sample 1) were calculated. The data are summarized in Table 5. With exception of 3-methyl-1-butanol, the mass transfer coefficients of the odorants are only marginally higher in rehydrated milk powder sample than in custard sample. The viscosity of the custard sample is much higher than the rehydrated milk powder sample (data not shown) and therefore one can conclude that the viscosity did not significantly influence the values of mass transfer coefficients of selected odorants (Table 5).

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