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Dynamic flavour release from Miglyol/water emulsions: modelling and validation

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Abstract

The initial dynamic flavour release from Miglyol/water emulsions was modelled. Modelling was merely based on theoretical physicochemical data of flavour volatiles and process parameters of a headspace apparatus used for model validation. The rate-limiting factor, determining initial flavour release, was the dynamic partitioning from the aqueous phase into the gas phase. This was experimentally confirmed by real time measurements of dynamic flavour release. Improved predictions of the model were obtained when theoretical octanol/water partition coefficients were replaced by measured Miglyol/water partition coefficients.

Keywords: Emulsion; Mouth; Dynamic flavour release; Miglyol; Modelling; logP

1. Introduction

The implication of fat on flavour release from food matrices is widely known (Hatchwell, 1996). Generally, flavour release decreases with increasing lipid level in the food matrix, with the exception of hydrophilic compounds possessing logP values near or below zero (Guichard, 2002). Lipid phases act as a reservoir for the aromas resulting in delayed release and perception. Fat-reduced or fat-free food matrices are characterised by a significantly changed aroma profile (Leland, 1997) and a generally disliked transient flavour burst (Hatchwell, 1994; Plug & Haring, 1993).

Aroma release from emulsions has received continuous attention. Application of static headspace methods has given insight into the partitioning of flavours between the liquid and the gaseous phase (Bakker, 1995; Piggott & Schaschke, 2001). However, flavour release in the mouth represents a dynamic situation (Taylor, 1996). Therefore, MS-nose techniques and the use of sophisticated release cells simulating mouth conditions have provided data of comparatively higher quality.

Apart from experimental data, static and dynamic flavour release from food matrices were successfully modelled (de Roos, 2000). Empirical models, using the method of quantitative structure–property relationship, led to predictions of volatile partitioning and dynamic flavour release (Katritzky, Wang, Sild, Tamm, & Karelson, 1998; Taylor & Linforth, 2001). Furthermore, semi-empirical (de Roos & Wolswinkel, 1994; Graf & de Roos, 1996; McNulty & Karel, 1973b) and theoretical (Banavara, Rabe, Krings, & Berger, 2002; Harrison, & Hills, 1997; Harrison, Hills, Bakker, & Clothier, 1997; McNulty & Karel, 1973a) models were established on the basis of theories of interfacial mass transfer, such as the penetration theory, the surface renewal theory, the boundary layer theory, or convective mass transfer. Although they satisfactorily explained the rate-limiting factors determining flavour release from various food matrices, many of the models focussed on single flavour compounds and/or were not supported by detailed experimentation.

The present work aimed at the modelling of initial flavour release from Miglyol/water emulsions within the first 30 s. Experimental data were used to confirm the validity of model predictions.

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Nomenclature

CMC	critical micelle concentration
Φ	oil fraction
SBSE	stir bar sorptive extraction
ANOVA	analysis of variance
DMR test	Duncan's multiple range test
$c_{hs}\ (t)$	volatile concentration in the headspace at any time t
c_0	initial volatile concentration in the bulk phase
k	mass transfer coefficient (m s^{-1})
A	interfacial area (m^2)
V_{hs}	volume of the headspace (m^3)
V_{water}	volume of the aqueous phase (m^3)
V_{oil}	volume of the oil phase (m^3)
c_{water}	volatile concentration in the water phase
c_{oil}	volatile concentration in the oil phase
V_{Miglyol}	volume of the Miglyol phase (m^3)
$K_{\mathrm{o/w}}$	oil/water partition coefficient
Re	Reynold's number
Sc	Schmidt's number
P	volatile permeability ($m^2\ s^{-1}$)
H_{ln}	logarithmic vertical distance in the reactor (m)
d	diameter of the stirrer (m)
n	number of rotations of the stirrer (s^{-1})
ρ	density of the bulkphase (kg m^{-3})
μ	dynamic viscosity of the bulkphase (kg $m^{-1}\ s^{-1}$)
D	diffusivity ($m^2\ s^{-1}$)
δ	effective film thickness of flowing air in contact with the bulkphase (m)
V_f	volumetric flow rate of air ($m^3\ s^{-1}$)
p	vapour pressure (Pa)
S	aqueous solubility (kg m^{-3})

2. Materials and methods

2.1. Materials

Emulsions consisted of water, Miglyol 812 (Sasol, Witten, Germany), and Tween 80 (Grünau, Illertissen, Germany). Diacetyl, isobutyl acetate, ethyl 2-methylbutyrate, *Z*-3-hexenyl acetate, 2,3-dimethyl pyrazine, *Z*-3-hexenol, 2-isobutyl thiazole, furfuryl acetate, linalool, 2-pentyl pyridine, D-carvone, β-damascenone and γ-nonalactone, each of analytical grade, were pre-dissolved in Miglyol or propylene glycol and added to the lipid phase of emulsions or water, respectively, resulting in concentrations typically present in beverages (Fenaroli, 1995; Table 1).

2.2. Emulsion preparation

Tween 80, at its critical micelle concentration (CMC), was dispersed in water (25 °C) using an Ultra-Turrax T50 (IKA, Staufen, Germany) operated with a dispersing tool (S 50 N—G45 F, IKA, Staufen, Germany) for fine dispersions at 10 000 rpm. The dispersion time was dependent on the sample volume: "30 s per l water". The CMC of the emulsifier for different oil levels in the emulsions was calculated with the help of Eq. (1), a linear regression equation recently found for the correlation between oil fraction (Φ) and CMC (Rabe, Krings, & Berger, 2003).

$$\mathrm{CMC}(\Phi) = 0.058\Phi + 1.245 \tag{1}$$

Flavours, pre-dissolved in Miglyol, were added to the bulk lipid phase (5, 10, 20, 50, 100 and 200 ml l^{-1}) which was pre-emulsified in the emulsifier/water solution using the Ultra-Turrax at "10 000 rpm for 30 s per l emulsion". Afterwards, homogenisation was done twice at 40 MPa, using a two pressure piston pilot plant homogeniser (APV Gaulin, Lübeck, Germany). The application of corresponding emulsifier CMCs and constant conditions of mechanical stress resulted in similar droplet sizes and distributions (Rabe et al., 2003). Of each emulsion 5 l volumes were prepared the day before measurement, transferred into closed glass bottles, and stored at room temperature for equilibration.

2.3. Determination of emulsion viscosity and emulsion density

Dynamic viscosity of the emulsions was measured using a Physica UDS 200 rheometer (Physica Messtechnik, Stuttgart, Germany). A constant shear rate of 150 s^{-1}, comparable to the shear force occurring in the mouth (van Vliet, 2002) and a linear temperature gradient from 25 to 40 °C were applied.

Density of emulsions was measured at 30 °C using a DMA 4500 density meter (Anton Paar, Graz, Austria).

2.4. Instrumentation

2.4.1. Gas chromatography–thermodesorption–flame ionisation detection (GC–TDS–FID)

Thermodesorption of the Tenax traps was carried out using a thermal desorption device (Gerstel TDS2, Mülheim an der Ruhr, Germany) mounted on a HP 6890 GC (Agilent Technologies, USA) equipped with a temperature programmable vapourisation inlet (Gerstel CIS 4 PTV, Germany). The PTV inlet incorporated a Tenax packed liner (Gerstel glass liners—TenaxTA, Germany) and was cooled by liquid nitrogen. Analytical conditions were as follows: thermal desorption: 30–260 °C at

Table 1
Emulsion concentrations, theoretical octanol/water partition coefficients and experimental Miglyov/water partition coefficients of the aroma compounds

Flavour	Concentration (mg l^{-1})	Theoretical $K_{\text{octanol/water}}$[a]	Experimental $K_{\text{Miglyol/water}}$
Diacetyl	0.784	0.05	0.04[c]
Isobutyl acetate	0.024	51.3	
Ethyl 2-methylbutyrate	0.029	182	
Z-3-Hexenyl acetate	0.383	407	
2,3-Dimethyl pyrazine	1.933	4.37	
Z-3-Hexenol	0.963	40.7	
2-Isobutyl thiazole	0.883	323	112[d]
Furfuryl acetate	0.978	12.3	24.6[d]
Linalool	0.972	1905	234[c]
2-Pentyl pyridine	1.463	2089	537[d]
D-Cavone	1.448	1175	159[d]
β-Damascenone	1.951	16,218	1778[d]
γ-Nonalactone	4.854	70.8[b]	79.4[d]

[a] From Banavara et al. (2002).

[b] Calculated with Advanced Chemistry Development (ACD) Solaris V 4.67 [(C) 1994–2002 ACD].

[c] Determined by SBSE followed by TDS-GC.

[d] Determined by direct injection of aqueous phase into a Tenax tube followed by TDS-GC.

60 °C min^{-1} and held for 8 min; splitless mode, 50 ml min^{-1} desorption gas flow (N_2), PTV: 1 °C (cryofocussing temperature) to 260 °C at 12 °C min^{-1} and held for 10 min; splitless; split mode (1/50) after 1.5 min; gas saver mode (1/20) after 3 min, column: 30 m×0.25 mm i.d.×0.25 μm INNOWAX (J&W Scientific); carrier gas flow 52 cm s^{-1} hydrogen; oven temperature, 40 °C (held for 1.5 min) to 130 °C at 4 °C min^{-1} to 180 °C at 8 °C min^{-1} to 250 °C at 25 °C min^{-1} and held for 10 min; detection, FID, 250 °C. Chromatograms were evaluated using HP ChemStation Software (Agilent Technologies, USA).

2.5. Determination of Miglyol/water partition coefficients

Partition coefficients of diacetyl and linalool were determined using a stir bar sorptive extraction (SBSE) method. Compounds were separately added to a separatory funnel each containing 100 ml of Miglyol and water resulting in concentrations of 0.784 mg l^{-1} and 0.972 mg l^{-1}, respectively. After vigorous shaking and an equilibration time of approximately 48 h, SBSE of an aliquot of the aqueous phase was done for 60 min using a Twister (Gerstel, Mülheim an der Ruhr, Germany) at 750 rpm. After the adsorption process, the stir bar was rinsed with deionised water, carefully dried with a tissue and thermodesorbed in a glass tube. External calibration was done for quantification.

For the determination of partition coefficients of furfuryl acetate, 2-isobutyl thiazole, 2,3-dimethyl pyrazine, 2-pentyl pyridine, β-damascenone and γ-nonalactone, approximately 2 (±0.005) g of each compound were transferred to a corresponding separatory funnel as described above. After equilibration, 2 μl of the aqueous phase were transferred into a Tenax trap which was subsequently thermodesorbed and analysed by GC-FID.

Each partition coefficient was determined at least in triplicate and calculated as the concentration ratio between the oil phase and the water phase.

2.6. Dynamic flavour release measurements

A mouth model apparatus was used for the measurement of dynamic flavour release from water and emulsions in the first 30 s (Rabe, Banavara, Krings, & Berger, 2002a). Dimensions and operating conditions were the same as reported recently (Rabe et al., 2003). Emulsion samples (5l) at 22 °C were introduced into the glass reactor of the apparatus. Within 3 s, a headspace of 850 ml was created above the emulsion. Simultaneously, a stirrer was started at 450 rpm, resulting in a shear rate of approximately 150 s^{-1}, comparable to the situation in the mouth (van Vliet, 2002) and a gas/liquid interfacial area of approximately 0.042 m^2 (Banavara et al., 2002). Then, subsequent on-line sampling of three 1.5 l headspace volumes, in high precision syringes at a volumetric flow rate of 9 l min^{-1} was done within 30 s. Thus, each headspace sample represents a 10 s time interval of flavour release. After the sampling process, the air samples were directed off-line through corresponding Tenax traps, using a vacuum pump at a flow of approximately 60–80 ml min^{-1}. Adsorbed volatiles were then thermodesorbed and analysed by GC-FID. Independent quantification was done by external calibration of each aroma molecule.

Each experiment was repeated at least three times.

2.7. Statistical analysis

Analysis of variance (ANOVA) was performed on release data. Duncan's multiple range (DMR) test was carried out to determine significant differences among mean values of flavour quantities released after 30 s. A significance level of $P < 0.05$ was applied throughout the study.

3. Results and discussion

3.1. Modelling flavour release from Miglyol/water emulsions

Dynamic flavour release from oil/water emulsions was shown to be highly dependent on the oil fraction existing in the continuous phase (Brauss, Linforth, Cayeux, Harvey, & Taylor, 1999; van Ruth, King, & Giannouli, 2002). On the other hand, emulsion parameters, such as droplet distribution, emulsifier molecules layering the oil droplets dissolved in the water phase and micelles formed by emulsifier molecules exceeding above the critical micelle concentration did not show a significant influence on the dynamic release process within the first 30 s (Rabe et al., 2003). These results were accordingly considered for the model developed in this study.

Before a bottle of liquid is opened, the emulsion is at equilibrium, and the flavour is stably partitioned between the aqueous and the lipid phase. As the aqueous phase forms the interface of the O/W emulsions with the headspace, flavour release occurs only from water. Therefore, the aroma fraction partitioned in the aqueous phase should be rate-limiting for release. Recently, initial flavour release from water was successfully modelled (Banavara et al., 2002), and the predictions were validated with data produced by the same equipment as applied in this study (Rabe et al., 2002a). The dynamic release process is described by Eq. (2), whose detailed derivation is given in the previous work (Banavara et al., 2002).

$$c_{\mathrm{hs}}(t) = c_0\left[1 - \mathrm{e}^{-k\frac{A}{V_{\mathrm{hs}}}t}\right] \tag{2}$$

The initial concentration is c_0, k is a mass transfer coefficient for forced convection in a stirred tank, A the interfacial area between air and water, t the time and V_{hs} the volume of the headspace. This correlation does not require any experimental input and enables the calculation of the headspace concentration c_{hs} with time (Banavara et al., 2002). According to the above consideration it was necessary to modify the original main Eq. (2) to adjust for the initial concentration of flavour in the aqueous phase.

$$K_{\mathrm{o/w}} = \frac{c_{\mathrm{oil}}}{c_{\mathrm{water}}} \tag{3}$$

$$c_0 V_{\mathrm{water}} = c_{\mathrm{water}} V_{\mathrm{water}} + c_{\mathrm{oil}} V_{\mathrm{oil}} \tag{4}$$

Based on Nernst's laws of partitioning given in Eqs. (3) and (4), the different volumes of the liquid phases V_{water} and V_{Miglyol}, as well as the partition coefficient of each volatile $K_{\mathrm{o/w}}$, between the lipid and the aqueous phases, were considered, leading to Eq. (5):

$$c_{\mathrm{hs}}(t) = \frac{c_0 V_{\mathrm{water}}}{V_{\mathrm{water}} + K_{\mathrm{o/w}} V_{\mathrm{Miglyol}}}\left[1 - \mathrm{e}^{-k\frac{A}{V_{\mathrm{hs}}}t}\right] \tag{5}$$

Table 2
Measured values of viscosity and density of emulsions containing different Miglyol amounts and the corresponding calculated Reynold's numbers (*Re*) in the reactor of the apparatus

Oil fraction (ml l^{-1})	Viscosity[a] (mPa s)	Density[a] (g ml^{-1})	*Re*[b]
0	2.23	0.996	16479
5	2.23	0.993	16423
10	2.25	0.992	16247
20	2.29	0.990	15976
50	2.38	0.988	15313
100	2.59	0.987	14096
200	2.96	0.985	12271

[a] Measured at 30 °C.
[b] Stirring speed: 450 rpm.

With the help of this modification, the initial flavour concentration, c_0, is reduced to the concentration in the aqueous phase of the emulsion. For the correction of viscosity and density changes by the different oil fractions of the emulsions, the corresponding values of these hydrodynamic parameters (Table 2) were incorporated in the Reynold's number, which characterises the flow of the liquid in the reactor and which is in turn part of the mass transfer coefficient k (Banavara et al., 2002):

$$k = 0.026(Re)^{0.8}(Sc)^{\frac{1}{3}}\frac{P}{H_{\mathrm{ln}}} \tag{6}$$

$$Re = \text{Reynold's number} = \frac{d^2 n\rho}{\mu} \tag{7}$$

$$Sc = \text{Schmidt's number} = \frac{\mu}{\rho D} \tag{8}$$

$$P = D\frac{\delta^2}{V_f}\sqrt{\frac{p}{S}} \tag{9}$$

P is a permeability term describing the migration of flavour molecules from the liquid to the gas phase (Banavara et al., 2002). H_{ln} is the logarithmic mean height and represents the average vertical distance which a flavour molecule has to travel through the liquid to reach the liquid/gas interface; d is the diameter of the stirrer used in the reactor, n the number of stirrer rotations, ρ the density of the liquid bulk phase, μ the dynamic viscosity of the liquid bulk phase, D the diffusion coefficient of a flavour molecule, δ the effective film thickness of air flowing at the liquid/gas interface, V_{f} the volumetric flow rate of air, p the partial pressure of a flavour molecule and S the solubility of a flavour molecule in water.

Mass transfer of volatiles through the liquid into the headspace is described by the Schmidt's number. As the release occurs from the water forming the interface in contact with the air, kinematic viscosity ($\mu\ \rho^{-1}$) of water and diffusion coefficients of flavour molecules (D) in water were applied in Eqs. (8) and (9).

3.2. Experimentally determined effect of oil fraction

Table 3 compares the released flavour quantities (after 30 s) from emulsions possessing different oil fractions.

Table 3
Influence of oil fraction on flavour release (μg after 30 s) from emulsions[a]

	Oil fraction [ml l^{-1}]						
Compound	0	5	10	20	50	100	200
Diacetyl	1.22ab±0.06	1.41bc±0.06	1.10a±0.12	1.24ab±0.02	1.50c±0.11	1.58c±0.15	1.78d±0.01
Isobutyl acetate	0.81a±0.01	0.49b±003	0.43c±0.00	0.37d±0.00	0.25e±0.00	0.16f±0.01	0.08g±0.01
Ethyl 2-methylbutyrate	1.22a±0.01	0.58b±0.06	0.44c±0.02	0.32d±0.01	0.17e±0.01	0.11ef±0.00	0.06f±0.01
Z-3-Hexenyl acetate	6.22a±0.22	2.04b±0.13	1.50c±0.10	0.99d±0.07	0.48e±0.01	0.33ef±0.03	0.16f±0.00
2,3-Dimethyl pyrazine	0.28a±0.00	0.34a±0.05	0.28a±0.03	0.32a±0.04	0.27a±0.01	0.34a±0.05	0.28a±0.00
Z-3-Hexanol	0.74ab±0.01	0.77b±0.03	0.68ac±0.05	0.71ab±0.05	0.60cd±0.00	0.66ad±0.07	0.44e±0.00
2-Isobutyl thiazole	4.50a±0.05	2.38b±0.22	1.82c±0.15	1.31d±0.10	0.67e±0.00	0.50e±0.06	0.25f±0.00
Furfuryl acetate	1.23a±0.07	1.02b±0.08	0.82c±0.06	0.77c±0.04	0.52d±0.01	0.44d±0.06	0.22e±0.01
Linalool	2.00a±0.10	0.85b±0.12	0.53c±0.03	0.38d±0.02	0.18e±0.00	0.13ef±0.03	0.06f±0.00
2-Pentyl pyridine	2.36a±0.14	0.53b±0.15	0.38bc±0.05	0.29c±0.05	0.24c±0.09	0.20c±0.07	0.28c±0.07
D-Carvone	1.31a±0.01	0.56b±0.11	0.38c±0.04	0.28d±0.03	0.14e±0.01	0.11e±0.02	0.07e±0.02
β-Damascenone	4.79a±0.43	0.39b±0.11	0.25b±0.02	0.21b±0.01	0.13b±0.04	0.19b±0.03	0.47b±0.25
γ-Nonalactone	0.11a±0.02	0.10ab±0.02	0.09ab±0.03	0.07bc±0.02	0.04c±0.00	0.05c±0.01	0.05c±0.01
CV[b][%]	4.2	13.4	9.2	8.8	6.9	13.8	6.6

[a] Values with different letters within a line are significantly different, ANOVA and DMR test ($P < 0.05$).

[b] Average coefficient of variation.

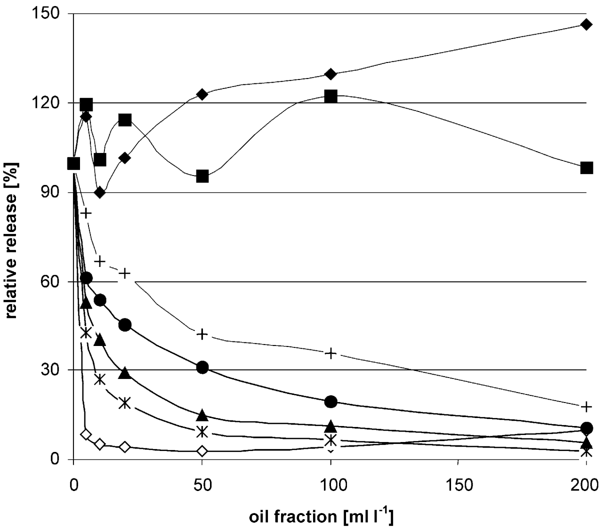

Fig. 1. Effect of oil fraction on flavour release from Miglyol/water emulsions relative to the release from water (◇, β-damascenone; *, linalool; ▲, 2-isobutyl thiazole; •, isobutyl acetate; +, furfuryl acetate; ■, 2,3-dimethyl pyrazine; ◆, diacetyl). Standard deviations of at least three replicates are given in Table 3.

Increasing oil levels in Miglyol/water emulsions led to decreasing accumulated flavour release rates for non-polar compounds (Fig. 1). The higher the octanol/water partition coefficient of these compounds (Table 1), the more distinctive was the impact of increasing oil fractions on the accumulated flavour release within the first 30 s (Fig. 1). Even small amounts of oil led to drastic shifts in phase partitioning and, correspondingly, to smaller concentrations released into the dynamic headspace (see for example β-damascenone in Fig. 1). The hydrophobic compounds approach a minimum of flavour release, which should represent the release from pure Miglyol. The octanol/water partition coefficient determines the characteristics of the approximation to this limit value. Hydrophilic compounds, such as 2,3-dimethyl pyrazine (logP, 0.64) and diacetyl (logP,−1.33) showed a different behaviour. The release of 2,3-dimethyl pyrazine was not influenced by increasing Miglyol fractions in the emulsion (Table 3, Fig. 1), showing that the partitioning of this compound remained unaffected. Applying an imaginary regression line in Fig. 1, considerable variance of the mean data points of accumulated dynamic release from the different emulsions is evident. This might be explained by the affinity for the aqueous phase of this molecule and the corresponding low absolute quantitative release increasing the analytical error (Table 3; Rabe et al., 2002a). Similar data were obtained in the case of diacetyl, where a slight increase in flavour release at Miglyol levels above 50 ml l^{-1} was found (Fig. 1). The kinetics of release from the emulsions for all flavour compounds were not affected by the oil level. Average linear regression coefficients of 0.99 indicated linear relationships between accumulated release and time for all flavours from water and each type of emulsion within the initial 30 s time course. Kinetics deviate from those of MS-nose measurements (cf. for example Brauss et al., 1999) but can be explained by mass transfer of flavours in and from the emulsions. First, constant release rates (accumulation led to the linear correlation with time) are due to the fast dynamic equilibration of volatiles from the aqueous phase, the comparably small headspace volume (0.85 ml), and the high air flow (9 l min^{-1}) through the reactor, providing a constant exchange of flavour enriched air during the simulation of constant drinking (Rabe et al., 2002a). Second, very low absolute amounts of flavour were released from water during the first 30 s (Rabe et al., 2002a). Flavour release rates, relative to the initial flavour concentration, ranged from 0.001 to 1.33%

depending on physicochemical properties of the flavours. As a result, the effective depletion of initial flavour concentration in the water, or in the water phase of the emulsion is too small to observe changing release rates. Additionally, mass transfer from the lipid phase into the water, in particular under stirring, is considered to be extremely fast (Harrison & Hills, 1997; Harrison et al., 1997), resulting in a rapid equalisation of concentration gradients. Third, the apparatus cannot yield nose-space data which are considerably influenced by complex processes of human physiology (dilution during tidal airflow, absorption and gradual desorption into/from the retronasal and nasal mucosa, absorption and desorption into/from a film formed by food residuals and saliva at the pharyngeal mucosa after swallowing) occurring during the retronasal flavour transport (Rabe et al., 2002a).

Mean coefficients of variation (CV) in Table 3 verified the good reproducibility of the apparatus used for release experiments, particularly with respect to the applied food-like, very low flavour concentrations (Table 1). The low CV values confirm the advantage of in vitro approaches to study the mechanisms of flavour release in comparison to MS-nose or sensory techniques, which are characterised by considerable variability, problems in flavour differentiation and, to some extent, lack of sensitivity (Brown & Wilson, 1996; Buettner & Schieberle, 2000; Buettner, Beer, Hannig, & Settles, 2001; Laing, 1994; Piggott & Schaschke, 2001). The variation in flavour release from water (4.2%) was smaller than from the emulsions (6.6–13.8%). This might be explained by the larger absolute flavour release into the headspace in the absence of a lipid phase.

Results reported in the literature are in accordance with the data presented in this study. Graf and de Roos (1996) and Carey, Asquith, Linforth, and Taylor (2002) showed the importance of small changes in the quantity of lipids, at very low lipid concentrations, on the product/air partitioning of volatiles in ice cream and cloud emulsions, respectively. Consistently, the octanol/water partition coefficient was determined to be the dominant physicochemical parameter affecting the process. Dynamic approaches (Brauss et al., 1999; Doyen, Carey, Linforth, Marin, & Taylor, 2001; Haahr, Bredie, Stahnke, Jensen, & Refsgaard, 2000; Jo & Ahn, 1999; van Ruth et al., 2002) and sensory studies (Brauss et al., 1999; Guyot, Bonnafont, Lesschaeve, Issanchou, Voilley, & Spinnler, 1996; Miettinen, Tuorila, Piironen, Vehkalahti, & Hyvönen, 2002) also revealed the decreasing effect of increasing oil levels on volatile release in emulsions for the majority of aroma compounds. A specific shift in the overall release profile, described by factors ranging from ~20 to ~1600 for single compounds, was recently shown in a comparison of volatile release from water and pure Miglyol (Rabe, Banavara, Krings, & Berger, 2002b). Comparing the static headspace of flavours above water and a 200 ml l^{-1} oil/water emulsion, the data of Schirle-Keller, Reineccius, and Hatchwell (1994) confirm the significant effect of lipids on changing aroma profiles. The present results underline the substantial change of the overall release profile when the fat content of a food matrix is reduced or even omitted, which may in turn change human flavour perception. Different liquid/liquid partition coefficients of flavour compounds and the properties of the lipid phase are mainly responsible for flavour imbalances and create the need for flavour reformulation in numerous food applications. To minimise such empirical work, Graf and de Roos (1996) successfully developed a non-equilibrium partition model to calculate reformulation factors for volatiles in ice creams of different fat levels and to restore the original flavour in a reduced fat product.

3.3. *Predicted versus experimental flavour release from Miglyol/water emulsions*

Figs. 2 and 3 show the comparison of predicted and experimental release (relative to the initial concentration in the bulk phase) of furfuryl acetate and diacetyl, and 2,3-dimethyl pyrazine and isobutyl acetate from Miglyol/water emulsions containing different oil fractions, respectively. Depending on the theoretically calculated octanol/water partition coefficients (Table 1) used in Eq. (5) instead of Miglyol/water partition coefficients, the predicted release is influenced by the oil fraction for the hydrophobic compounds and approaches a minimum value with increasing oil levels, which is in agreement with the experimental data. Furthermore, the steady state in the case of hydrophilic 2,3-dimethyl pyrazine and diacetyl is also correctly predicted (Figs. 2 and 3). In general, the course of release of every compound used in the study is well described by the model. Deviations from the experimental data were small, although partly not within the confidence interval of the replicated experiments. This is

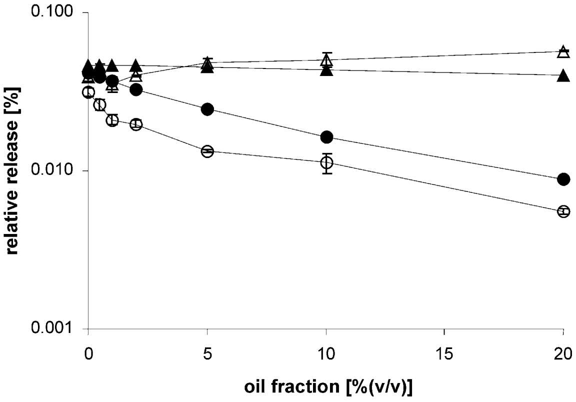

Fig. 2. Comparison of model-predicted (solid symbols) and experimental (open symbols) release of furfuryl acetate (●) and diacetyl (▲) from emulsions containing different oil fractions. Accumulated volatile amounts released within the first 30 s were compared.

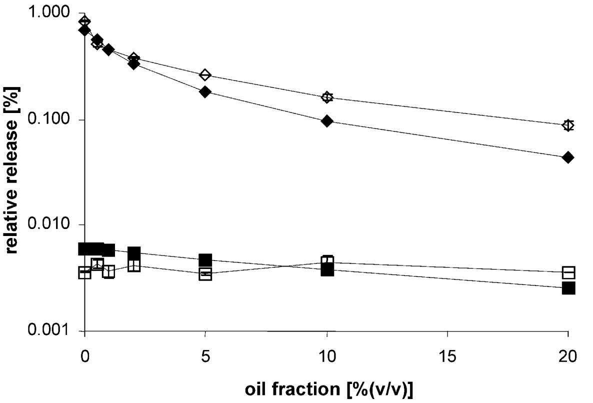

Fig. 3. Comparison of model-predicted (solid symbols) and experimental (open symbols) release of 2,3-dimethyl pyrazine (■) and isobutyl acetate (◆) from emulsions containing different oil fractions. Accumulated volatile amounts released within the first 30 s were compared.

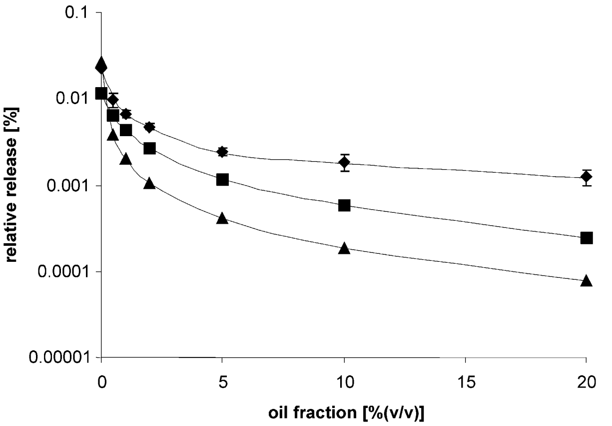

Fig. 5. Comparison of experimental (◆) and model-predicted release (cumulative, 30 s) of D-carvone. Predictions were calculated using theoretical octanol/water partition coefficients (▲) or experimental Miglyol/water partition coefficients (■).

due to error propagation of the deviations obtained in the previous work (Banavara et al., 2002): theoretically calculated variables of the permeability term [Eq. (9)], namely diffusivity, partial pressure, solubility and effective film thickness of the air flowing at the air/water interface, incorporated in the mass transfer coefficient [Eq. (6)] of the previous model, resulted in small deviations from reality. However, deviations are sufficiently small for practical applications, and the reasonably parallel tendency of theoretical and experimental release curves indicates that the error described above should be similar for every predicted data point (Figs. 2 and 3). Deviations are in the same order of other models which were, in contrast to the present study, empirically fitted to experimental data generated previously (Nahon, Harrison, & Roozen, 2000). Using experimental Miglyol/water partition coefficients (Table 1) for compounds showing comparably high deviations between experimental and theoretical data instead of theoretical octanol/water partition coefficients, led to a considerable improvement of the model predictions. Figs. 4 and 5 clearly demonstrate the improved fit of predicted and experimental release curves for linalool and D-carvone, respectively. This amendment might be explained by recent results on the influence of the chemical composition of lipids on the initial flavour release from emulsions (Rabe et al., 2003). The data suggested that lipid composition and the molarity of the lipid phase are important for the liquid/liquid partitioning process under static and dynamic conditions. Therefore, according to Eq. (5) initial flavour release is considerably affected, as the initial concentration in the water phase is changed.

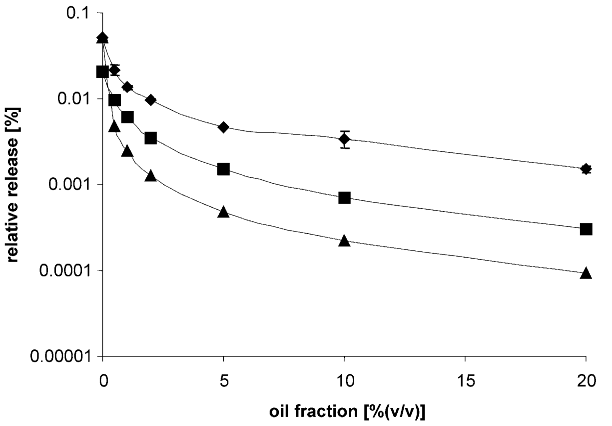

Fig. 4. Comparison of experimental (◆) and model-predicted release (cumulative, 30 s) of linalool. Predictions were calculated using theoretical octanol/water partition coefficients (▲) or experimental Miglyol/water partition coefficients (■).

4. Conclusion

Flavour release kinetics from emulsions within the first 30 s of simulated drinking were measured with a computerised apparatus, applying the ‘from zero start’-technique (Rabe et al., 2002a). Experimental data were used for the validation of a model independently derived from theoretical physicochemical constants of flavour compounds and some parameters of the environment surrounding the emulsion, i.e. the apparatus used for validation. In comparison to other models, the advantage of the model equation of this paper [Eq. (5)] is the complete omission of experimental data input, with the exceptions of emulsion density and viscosity, which are, however, easy to measure. The applicability of the model proved the assumption that the initial dynamic flavour release from emulsions is dominated by the phase partitioning of the volatiles and, consequently, the flavour concentration in the aqueous phase. The use of experimental partition coefficients instead of theoretical octanol/water partition coefficients and recent results on the influence of the chemical composition of lipids on flavour release (Rabe et al., 2003), indicated that the generally used octanol/water partition coefficient should not be considered as a reliable parameter for describing the polarity of all lipids. In fact, individual partition coefficients for different lipids seem to be necessary for the precise description of flavour partitioning in emulsions and, consequently, initial dynamic flavour release within the first 30 s. Ongoing studies are underway which are focused on this topic.

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