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Dynamic Flavor Release from Sucrose Solutions

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The initial dynamic flavor release from sucrose solutions was modeled. Modeling was based on the theoretical hydration behavior of sucrose, theoretical physicochemical data of flavor volatiles, and process parameters of a headspace apparatus used for model validation. The rate-limiting factor determining the initial flavor release was the hydration of sucrose, which in turn depends on the molarity of sucrose in the solution and, therefore, on the actual amount of nonbound water. Improved solubility of the more hydrophilic compounds due to their orientation toward the hydration shells of the sugar molecules was considered. The viscosity of nonassociated water forming the microregion for mass transfer of volatiles was considered instead of the bulk solution viscosity. Experimental validation of the model by real-time measurements of dynamic flavor release using foodlike flavor concentrations confirmed the above theory. Increasing sucrose concentrations resulted predominantly in increased flavor release, and bulk solution viscosity showed no effect.

KEYWORDS: Adsorption; dynamic flavor release; hydration; modeling; mouth; sterical hindrance; sucrose

INTRODUCTION

Despite the actual trend toward low-energy foods, a large number of beverages contain considerable amounts of sucrose (e.g., regular soft drinks). The importance of synergistic cognitive effects between flavor perception and sugar was shown by Davidson et al. (1), who analyzed the timing of flavor and tastant delivery from chewing gum. Dalton et al. (2) demonstrated the effect of a sweetener on flavor perception. Sensorial experiments showed that test persons perceived dissolved aromas, which were present in concentrations below their odor thresholds, after the addition of saccharin. According to these results, it is of interest to what extent sucrose influences flavor release from liquids in the mouth and, subsequently, flavor perception. The literature offers inconsistent data, with flavor release being either enhanced or suppressed upon the addition of sucrose to water. In particular, the latter effect was ascribed to increasing solution viscosity and binding phenomena between volatiles and the sugar. On the other hand, increasing release rates were discussed on the basis of the "salting out" effect.

The aim of the present study was the modeling of initial dynamic flavor release from sugar solutions, the experimental validation of predicted data, and, ultimately, a better insight into parameters and mechanisms affecting flavor release from liquids under simulated mouth conditions.

MATERIALS AND METHODS

Model Flavor Mix. Thirteen aroma compounds from different chemical classes, diacetyl, isobutyl acetate, ethyl 2-methylbutyrate,

(Z)-3-hexenyl acetate, 2,3-dimethylpyrazine, (Z)-3-hexenol, 2-isobutylthiazole, furfuryl acetate, linalool, 2-pentylpyridine, D-carvone, β -damascenone, and γ -nonalactone (Symrise, Holzminden, Germany), each of analytical grade, were predissolved in propylene glycol (PG; Symrise) at different concentration levels (Table 1) to give a 10% (w/w) flavor mix/PG stock solution for flavor release experiments.

Preparation of Sucrose Solutions. Solutions of sucrose (Sigma-Aldrich, Steinheim, Germany) at 50, 200, 375, and 500 g L⁻¹ were prepared by adding solutes stepwise to tap water under vigorous stirring. Prior to the start of flavor release experiments, water or solutions were equilibrated at 26 °C, and 1 g of the flavor premix was added to 5 L of each liquid, resulting in the foodlike concentrations (3) listed in Table 1.

Determination of Solution Viscosity and Solution Density. The dynamic viscosity of sucrose solutions 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 (4) and a linear temperature gradient from 25 to 40 °C were applied.

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

Dynamic Flavor Release Measurements. A mouth model apparatus was used for the measurement of dynamic flavor release from water and solutions in the first 30 s (3). Dimensions and operating conditions, representing up-scaled mouth conditions, were the same as reported in the previous work and provided high reproducibility and sensitivity. Five liters of liquid was introduced into the glass reactor of the apparatus. Within 3 s, a headspace of 850 mL was created above the liquid. Simultaneously, a stirrer was started at 450 rpm, resulting in a shear rate of ~ 150 s⁻¹ (3), comparable to the situation in the mouth (4), and a gas/liquid interfacial area of ~ 0.042 m² (5). Then, subsequent on-line sampling of three 1.5 L headspace volumes in high-precision syringes at a volumetric air flow rate of 9 L min⁻¹ was done within 30 s. Thus, each headspace sample represented a 10 s time interval of

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Table 1. Composition of the Flavor Mix, Final Concentrations, and Log *P* Values of the Single-Flavor Compounds

flavor compound	portion in the flavor mix (%)	final concn (mg L ⁻¹)	log <i>P</i> ^a
diacetyl	2.47	0.41	-1.33
isobutyl acetate	0.06	0.010	1.71
ethyl 2-methylbutyrate	0.05	0.009	2.26
(<i>Z</i>)-3-hexenyl acetate	1.97	0.32	2.61
2,3-dimethylpyrazine	7.40	1.21	0.64
(<i>Z</i>)-3-hexenol	4.98	0.81	1.61
2-isobutylthiazole	4.23	0.69	2.51
furfuryl acetate	4.99	0.82	1.09
linalool	4.92	0.81	3.28
2-pentylpyridine	7.40	1.21	3.32
D-carvone	7.38	1.21	3.07
β-damascenone	29.51	4.83	4.21
γ-nonalactone	24.63	4.03	1.85 ^b
initial total flavor	100.00	16.37	

^a Reference 5. ^b Calculated with Advanced Chemistry Development (ACD) software, Solaris v 4.67 (ACD, 1994–2002).

flavor release. After the sampling process, the air samples were directed off-line through corresponding Tenax traps using a vacuum pump at a flow of ~60–80 mL min⁻¹. Adsorbed volatiles were then thermodesorbed and analyzed by GC-FID. Independent quantification was done by external calibration of each aroma compound. For data treatment and comparison, quantified flavor amounts of the three traps were cumulated, representing absolute flavor release after 30 s (at *t* = 0, all headspace concentrations are 0).

Instrumentation. Thermodesorption–Gas Chromatography–Flame Ionization Detection (TDS-GC-FID). Thermodesorption of the Tenax traps was carried out using a thermal desorption device (Gerstel TDS 2, Mülheim an der Ruhr, Germany) mounted on an HP 6890 GC (Agilent Technologies), equipped with a temperature-programmable vaporization inlet (Gerstel CIS 4 PTV) and a FID. The PTV inlet incorporated a Tenax-packed liner (Gerstel glass liners, TenaxTA) and was cooled by liquid nitrogen. The TDS 2 was heated from 30 to 260 °C thermodesorption temperature at 60 °C min⁻¹, and desorption was done for 8 min using a desorption gas (N₂) flow of 50 mL min⁻¹. During thermodesorption the PTV was cooled at 1 °C, whereas its temperature was raised to 260 °C at 12 °C min⁻¹ and held for 10 min after the desorption process. Splitless mode was initially applied, and split modes of 1/50 and 1/20 (gas saver mode) after 1.5 and 3 min, respectively, were used. The column used was a 30 m × 0.25 mm i.d. × 0.25 μm Innowax (J&W Scientific) operated with a carrier gas flow (H₂) of 52 cm s⁻¹. The oven temperature program was as follows: from 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. The FID was operated at 250 °C. Chromatograms were evaluated using HP ChemStation software (Agilent Technologies).

Statistical Analysis. Analysis of variance (ANOVA) was performed on flavor release data from sucrose solutions. Fisher's least significant difference (LSD) test at a significance level of *p* < 0.01 was carried out to determine significant differences among mean values of flavor quantities released after 30 s.

RESULTS AND DISCUSSION

Modeling Flavor Release from Sucrose Solutions. Solubilization of sucrose in water is associated with the formation of hydration shells of water surrounding the solute molecules (6). Depending on the solute concentration and the corresponding water/solute interactions (for example, dipole–dipole interactions, hydrogen bonding, or van der Waals forces), and, therefore, the strength of water binding to the solute, the ratio between free (nonassociated) and bound (associated) water should decrease with increasing solute concentrations. Assuming

Table 2. Constants Used for the Calculation of Flavor Release from Solutions

constant	setting	constant	setting
<i>A</i>	0.0405 m ²	<i>μ</i>	cf. Table 4
<i>V</i> _{hs}	0.00085 m ³	<i>D</i>	see ref 5
<i>H</i> _{ln}	0.15 m	<i>δ</i>	0.00175 m
<i>d</i>	0.07 m	<i>V</i> _f	0.00016 m ³ s ⁻¹
<i>n</i>	7.5 s ⁻¹	<i>p</i>	see ref 5
<i>ρ</i>	cf. Table 4	<i>S</i>	see ref 5

flavor release to occur solely from the nonassociated water phase and the nonexistence of flavor adsorption to the hydrated sucrose, the initial flavor concentration in the “free water” fraction should increase with increasing solute concentration due to the decreased volume of nonassociated water.

Modeling of initial dynamic flavor release from water (5) showed good agreement with experimental data provided by the computerized apparatus applied in this study (3).

$$c_{hs}(t) = c_0[1 - e^{-k(A/V_{hs})t}] \quad (1)$$

Initial dynamic flavor release from water is described by eq 1, with *c*_{hs} being the flavor concentration in the headspace with time *t*, *c*₀ the initial flavor concentration in the bulk liquid phase, *k* the mass transfer coefficient for forced convection in a stirred tank, *A* the interfacial area between air and water, and *V*_{hs} the volume of the headspace.

$$k = 0.026(\text{Re})^{0.8}(\text{Sc})^{1/3}(P/H_{ln}) \quad (2)$$

Equation 2 was initially derived from the mass transfer correlation for forced convection in a circular tube under turbulent flow (5): *k* comprises the Reynold's number (Re), characterizing the input and absorption of shear forces into/by the bulk solution, the Schmidt's number (Sc), a parameter describing the mass transport of volatiles through the bulk liquid, a permeability term *P*, comprising physicochemical properties of flavor molecules as well as characteristics of the air stripping the headspace above the liquid, and *H*_{ln}, the logarithmic mean height representing the average vertical distance a flavor molecule has to travel through the liquid to reach the gas/liquid interface.

$$\text{Re} = d^2 n \rho / \mu \quad (3)$$

$$\text{Sc} = \mu / (\rho D) \quad (4)$$

$$P = D(\delta^2/V_f)\sqrt{p/S} \quad (5)$$

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 flavor molecule in water, *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 flavor molecule, and *S* the solubility of a flavor molecule in water. Table 2 lists the values of the different variables used in the model.

If, according to the above derivation, the rate-limiting factor for initial flavor release is the volume of nonassociated water present for the solubilization of volatiles, eqs 1 and 2 have to be modified. The effective increase of the initial flavor

Table 3. Empirical and Reported Hydration Numbers of Sucrose at Different Solute Concentrations and Resulting Initial Flavor Concentrations in the Free Water Phase

solute concn (g L ⁻¹)	initial flavor concn in the nonassociated water phase ^a (mg L ⁻¹)	h_n	
		lit.	empirical
0	16.37		
50	20.38	~21 ^b ~37 ^c	73
200	26.19	~5 ^d	30
375	54.34	~5 ^d	27
500	109.09	<5 ^d	22

^a Derived from eq 6. ^b Reference 29. ^c Reference 22. ^d Reference 6.

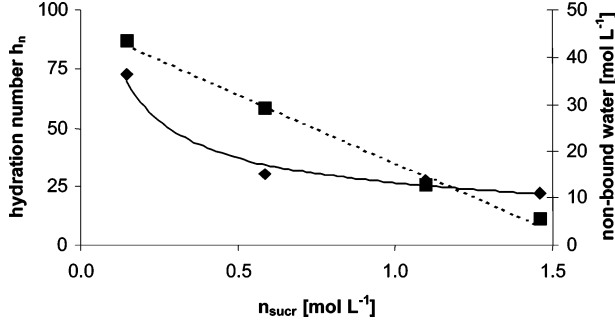


Figure 1. Correlation between sucrose concentration in solutions and hydration numbers of sucrose molecules (◆) and corresponding fractions of nonassociated water (■).

concentration in the free water phase is calculated with the help of eq 6:

$$c_{0,\text{sucr}} = c_0 a \quad (6)$$

$$a = n_{w,t} / (n_{w,t} - n_{w,b}) \quad (7)$$

$$n_{w,t} = \frac{(V_{re} - V_{hs})\rho - m_{\text{sucr}}}{18} \quad (8)$$

$$n_{w,b} = n_{\text{sucr}} h_n \langle n_{\text{sucr}} \rangle \quad (9)$$

The initial concentration c_0 (eq 1) is extended by a factor a , the total water of the solution divided by the free water fraction (eq 7), resulting in $c_{0,\text{sucr}}$, the initial flavor concentration in the nonassociated water phase of sucrose solutions. $n_{w,t}$ is the number of moles of total water in the solution and is derived from eq 8, with V_{re} being the volume of the reactor (5 L) and m_{sucr} the total mass of sucrose in the solution. $n_{w,b}$ of eq 7 represents the mole number of water associated with the sucrose molecules in the solution and is defined in eq 9 as the product of n_{sucr} , which is the mole number of sucrose dissolved in the solution and the hydration number h_n representing the number of water molecules hydrating one sucrose molecule. Empirical hydration numbers for various sucrose concentrations were used for predictions (Table 3). A potential correlation between n_{sucr} and h_n with a regression coefficient R^2 of 0.9675 was found (Figure 1). Equation 10 represents this correlation:

$$h_n \langle n_{\text{sucr}} \rangle = 26.2 n_{\text{sucr}}^{-0.51} \quad (10)$$

Consideration of the above modifications resulted in increased effective initial flavor concentrations $c_{0,\text{sucr}}$ with increasing sucrose concentrations in the nonassociated water phase (Table

Table 4. Measured Values of Viscosity and Density of Sucrose Solutions and the Corresponding Calculated Reynold's Numbers (Re) in the Reactor of the Apparatus

concn (g L ⁻¹)	viscosity ^a (mPa s)	density ^a (g mL ⁻¹)	Re ^b
0	2.23	1.00	16598
50	2.35	1.02	16023
200	2.50	1.04	15317
375	4.50	1.14	9291
500	7.45	1.18	5827

^a Measured at 30 °C. ^b Stirring speed = 450 rpm.

3). Therefore, eq 11 was used for the prediction of initial flavor release from sucrose solutions:

$$c_{\text{hs}}(t) = c_{0,\text{sucr}} [1 - e^{-k(A/V_{\text{hs}})t}] \quad (11)$$

As Re describes the shear force absorption of the whole solution, changing kinematic viscosity ($\rho \mu^{-1}$) with increasing sucrose concentrations was considered. Table 4 lists the corresponding values of μ , ρ , and the resulting Re in the reactor during experiments. On the other hand, all parameters involved in mass transfer, namely, ρ and μ of Sc, D , p , and S , are related to pure water because of the basic assumption.

Experimentally Determined Effect of Sucrose Concentration. Experimental data of flavor release from sucrose solutions at different concentrations are summarized in Table 5. Six of the volatiles, namely, (Z)-3-hexenyl acetate, 2-isobutylthiazole, furfuryl acetate, linalool, D-carvone, and γ -nonalactone, showed an increasing, partly significant trend with increasing sugar concentrations (ANOVA and LSD test, $p < 0.01$). Diacetyl, 2,3-dimethylpyrazine, (Z)-3-hexenol, and 2-pentylpyridine showed a similar behavior at sucrose concentrations ranging from 0 to 375 g L⁻¹ and β -damascenone from 50 to 500 g L⁻¹, respectively (Table 5). Isobutyl acetate and ethyl 2-methylbutyrate showed dissenting, fairly constant flavor release rates with increasing sucrose concentrations, and effects were not significant according to ANOVA and LSD test ($p < 0.01$). As with other liquid matrices of different viscosities, for example, water (3), neutral oil (7), emulsions (8), thickened emulsions (9), or sodium chloride solutions (10), a linear relationship between accumulated initial flavor release and time was obtained under experimental conditions similar to those applied in this study. Linear regression coefficients ranging from 0.991 to 1 were independent of sucrose concentration (data not shown). Replicates, in particular, at high sucrose concentrations, showed larger variability than in previous studies conducted on water (3), aqueous solutions of sodium chloride (10), and emulsions (8). As a result, less significant differences in flavor release between solutions containing different concentrations of sucrose were detected using the LSD test, despite its being the least conservative post hoc test (11). Table 5 indicates a correlation between sucrose concentration and the average coefficients of variation (CV): the higher the solute concentration, the higher the CV.

Hansson et al. (12) also experienced higher variability in flavor release when applying high sucrose concentrations >20% (w/w). Using static headspace measurements they showed an increasing effect of increasing sucrose concentrations on flavor release from a soft drink related model system. Kieckbusch and King (13) and Godshall (14) reported the same behavior for straight-chain acetates and for alcohols, ketones, and esters, respectively. Roberts et al. (15) found the opposite when analyzing dynamic flavor release by applying a stirred glass vessel directly connected with a quadrupole mass spectrometer

Table 5. Influence of Sucrose Concentration on Flavor Release (Micrograms, after 30 s) from Aqueous Solutions^a

flavor compound	sucrose concn (g L ⁻¹)				
	0	50	200	375	500
diacetyl	0.65a ± 0.00	0.82ab ± 0.07	0.85ab ± 0.14	0.97b ± 0.10	0.69ab ± 0.11
isobutyl acetate	0.36a ± 0.01	0.44a ± 0.09	0.48a ± 0.17	0.42a ± 0.16	0.27a ± 0.18
ethyl 2-methylbutyrate	0.46a ± 0.02	0.52a ± 0.02	0.50a ± 0.08	0.45a ± 0.17	0.41a ± 0.27
(Z)-3-hexenyl acetate	6.69a ± 0.05	7.91a ± 0.39	9.04a ± 0.94	10.33a ± 1.55	19.80b ± 4.50
2,3-dimethylpyrazine	0.23a ± 0.02	0.25a ± 0.04	0.28a ± 0.02	0.33a ± 0.07	0.24a ± 0.03
(Z)-3-hexenol	0.79a ± 0.06	0.91a ± 0.07	1.11ab ± 0.03	1.47b ± 0.23	1.35b ± 0.26
2-isobutylthiazole	4.40a ± 0.02	5.02a ± 0.41	5.23a ± 0.57	5.50a ± 0.03	8.09b ± 1.41
furfuryl acetate	1.32a ± 0.06	1.40a ± 0.15	1.80ab ± 0.08	2.04ab ± 0.46	2.47b ± 0.56
linalool	2.11a ± 0.07	2.30a ± 0.25	3.05ab ± 0.30	4.22b ± 1.01	8.06c ± 0.90
2-pentylpyridine	2.69a ± 0.62	3.11a ± 0.93	3.25a ± 0.92	3.95a ± 0.26	3.58a ± 1.06
o-carvone	1.42a ± 0.13	1.47a ± 0.26	1.76a ± 0.34	2.26a ± 0.38	3.53b ± 0.56
β-damascenone	16.06ab ± 4.81	14.67a ± 5.62	19.17ab ± 7.26	21.52ab ± 3.00	27.16b ± 4.99
γ-nonalactone	0.16a ± 0.01	0.19ab ± 0.06	0.19ab ± 0.04	0.28b ± 0.01	0.30b ± 0.06
CV ^b (%)	7.5	15.9	16.7	17.6	26.2

^a Values with different letters within a row are significantly different (ANOVA and LSD test, both at $p < 0.01$). ^b Average coefficient of variation.

(16). They reported decreasing flavor release rates (maximum intensities after time periods of several minutes were compared) with increasing sucrose concentrations for a variety of aromas and proposed bulk viscosity and binding to be important for flavor retention. De Roos and Wolswinkel (17) found the effect of sucrose to be generally small, and only hydrophobic compounds were preferentially retained in a 25% sucrose solution in comparison to water. Nahon et al. (18), Friel et al. (19), and Nahon et al. (20) grouped aroma molecules in three categories. In the first group, flavor release was not influenced by sucrose concentration. The second group showed a positive correlation between release and sucrose content, and a negative correlation between the two variables was obtained for a third group. Furthermore, Nahon et al. (18) reported a correlation between the grouping and the gas chromatographic retention times of the compounds dynamically released during experiments. Flavor compounds with short retention times showed increased release rates, whereas compounds with medium and long retention times were not or negatively influenced by increasing sucrose concentrations, respectively.

Predicted versus Experimental Flavor Release from Sucrose Solutions. In accordance with the data obtained with the initial mathematical model for the prediction of flavor release from water (5), predicted release kinetics in the present study were linear for all flavor compounds at all sucrose concentrations (data not shown). **Figure 2** shows the comparison of experimental and predicted initial dynamic flavor release from sucrose solutions of hydrophobic (cf. **Table 1**) linalool, 2-isobutylthiazole, β-damascenone, and (Z)-3-hexenyl acetate after a time period of 30 s. The increasing effect of water binding sucrose is properly described by the model predictions, indicated by the fairly parallel run of the curves. Deviations from experimental data are constant with the exception of 500 g L⁻¹ sucrose concentration data and, additionally, the 375 g L⁻¹ sucrose concentration data point in the case of 2-isobutylthiazole. Predictions out of the confidence interval of experimental data may be due to the error propagation of the original model derived for the prediction of flavor release from water (5). Physicochemical data of volatiles, namely, diffusivity D , partial pressure p , and aqueous solubility S (eqs 4 and 5), were theoretically calculated and may cause deviations from experimental results (cf. ref 8). The considerable increase of the slope of the experimental release curves in **Figure 2** indicates the under-run of a critical volume of water available for the hydration and solubilization of flavors at sucrose concentrations > 375 g L⁻¹. As a result, a significant increase of released flavor

was obtained (**Table 5**, ANOVA and LSD test at $p < 0.01$). Variability of experimental data at high sucrose concentrations may indicate a competition between sucrose and aroma molecules for water of hydration. Furthermore, sucrose/sucrose interactions via hydrogen bonds (6) were shown to influence molecular mobility. According to Richardson et al. (21), the mobility of sucrose/water systems decreased in particular at high sucrose concentrations > 40%. Thus, the CV values given in **Table 5** represent the complexity of hydration processes at high solute concentrations.

Table 3 lists empirical h_n values used for the prediction of flavor release at various sucrose concentrations, as well as h_n values given in the literature. Starzak et al. (6) compared and assessed existing hydration number and water activity models for sucrose in water. They reported average h_n given in the literature to range from 1.8 determined using NMR to 21 obtained by near-infrared spectrometry. However, an average h_n of five water molecules surrounding one molecule of sucrose for medium sucrose concentrations was indicated by a large number of theoretical studies. Engelsen and Pérez (22) reported 37.6 water molecules within the hydration shell for highly diluted sucrose solutions as a result of their 500 ps molecular dynamics simulation. At very high solute concentrations > 40% (w/w), h_n values of < 5 were postulated (6). Application of the reported h_n in the model was not satisfying, as predictions considerably deviated from experimental results. Empirical h_n values were applied in eq 9; the decreasing trend at increasing concentrations of sucrose agrees with literature data (**Table 3**). h_n values given in the literature are consistently smaller than those used for model predictions. The empirical step for the model derivation in this work, however, is valid for all flavor molecules and classes studied. Results of the present work therefore indicate that a considerable number of additional water molecules, oriented and weakly bound to the outer hydration shell, are involved in sucrose solubilization.

The experimental and theoretical release of the more hydrophilic (cf. **Table 1**) diacetyl, 2,3-dimethylpyrazine, furfuryl acetate, and (Z)-3-hexenol from sucrose solutions is shown in **Figure 3**. Up to sucrose concentrations of 200 g L⁻¹ the increasing trend in release of these compounds is correctly predicted by the model. In contrast to the model predictions, compounds showed no further increase in flavor release at concentrations ≥ 375 g L⁻¹. The compounds depicted in **Figure 3** compete with sucrose for water of hydration at high concentrations more successfully than the nonpolar volatiles shown in **Figure 2**. Additionally, flavor/sucrose interactions may

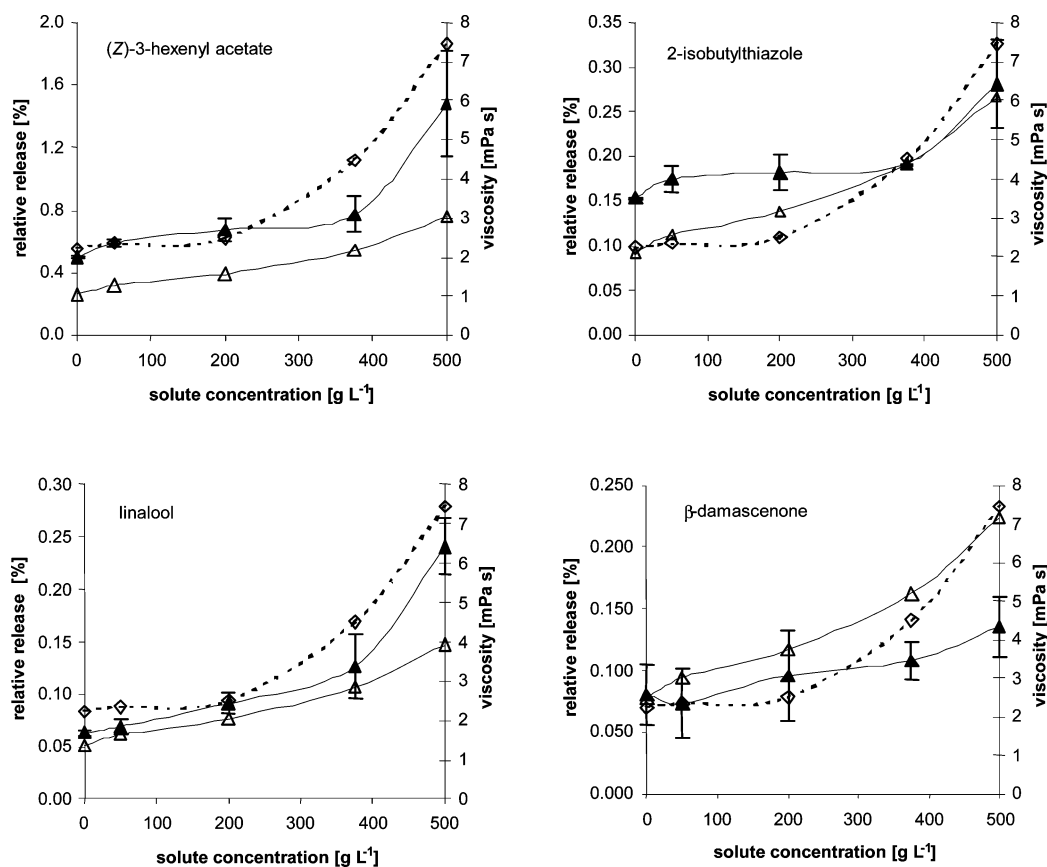


Figure 2. Comparison of model predicted (Δ) and experimental (▲) volatile release from sucrose solutions after 30 s. The second ordinate represents the viscosity of sucrose solutions (◇).

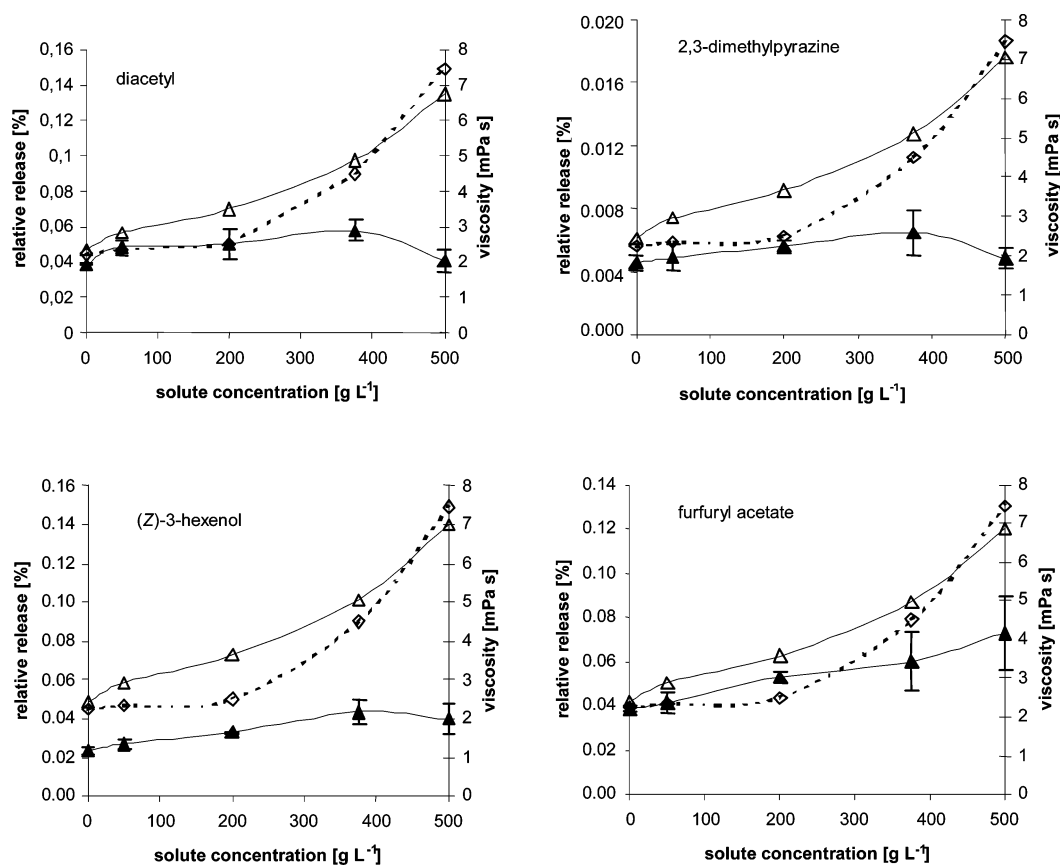


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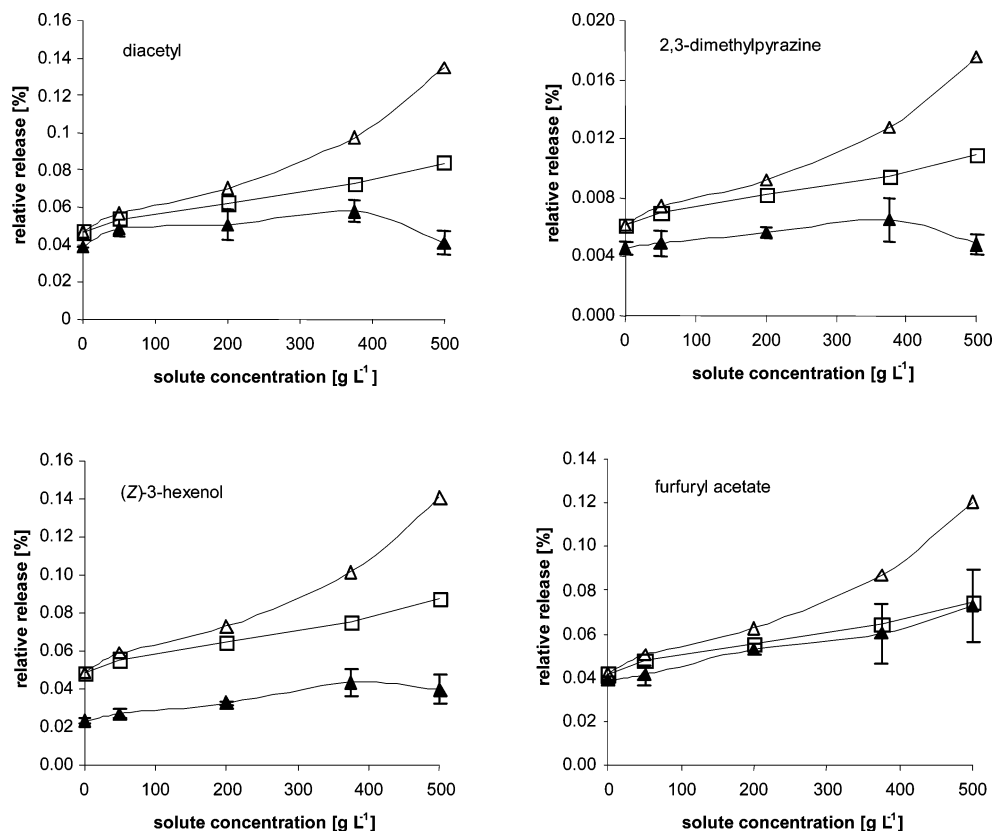


Figure 4. Comparison of model predicted (open symbols) and experimental (\blacktriangle) volatile release from sucrose solutions after 30 s, with (\square) and without (\triangle) consideration of eq 13 in eq 5.

occur at high sucrose concentrations (23). Large coefficients of variation of experimental data indicate again the considerable variability of hydration and/or orientation/adsorption processes at high solute concentrations.

Polarity of Sucrose Affects the Aqueous Solubility and Release of Flavors. A similar situation was found in the case of sodium chloride (10). In particular, at high solute concentrations ions force more hydrophilic compounds possessing $\log P < 2.4$ to be retained in the solution due to ion–dipole interactions resulting in comparably decreased flavor release. The improved solubility was accordingly considered in the volatile permeability term P by modification of the flavor’s aqueous solubility S (10):

$$S_{\text{NaCl}} = S f_1^z \quad (12)$$

Depending on the ratio f_1 between the volume of the salt solution and the corresponding volume of free water extended by an exponent z characterizing the flavor compound’s hydrophilicity, S of hydrophobic compounds ($\log P > 2.4$) remained constant ($z = 0$), whereas S of hydrophilic compounds ($\log P < 2.4$) increased by the square root of f_1 ($z = 0.5$), resulting in S_{NaCl} , the modified aqueous solubility of flavors in sodium chloride solutions. The same approach was applied for the present sucrose model:

$$S_{\text{sucr}} = S a^z \quad (13)$$

S_{sucr} represents the aqueous solubility of flavors in sucrose solutions. The same $\log P$ limit and corresponding z values as in the previous work (10) were valid and applied in the present model, resulting in considerably improved predictions. **Figure 4** compares experimental and calculated release data with and without consideration of modified S_{sucr} of the hydrophilic

compounds depicted in **Figure 3**. Their improved solubility, in particular, at high solute concentrations, is obvious. As in the case of electrolytes, hydrophilic volatiles possessing considerable dipoles orient themselves toward the hydration spheres of the sugar molecules, especially at decreasing h_n .

Effect of Viscosity on Dynamic Flavor Release. **Figures 2 and 3** indicate increasing viscosity of sucrose solutions going along with both increasing experimental and predicted release data of 11 of 13 volatiles (cf. **Table 5**). A different behavior was obtained only for isobutyl acetate and ethyl 2-methylbutyrate, which showed a steady release through the entire range of solute concentrations (**Table 5**). These results differ from the current opinion that mass transfer of flavors through matrices decreases with increasing viscosity. de Roos and Wolswinkel (17), for example, considered viscosity to be an important factor influencing mass transfer through liquids. Bakker et al. (24) found the dynamic release of diacetyl from liquid gelatin to be negatively correlated with solute concentration and corresponding viscosity in both, experiments and theoretical considerations, when applying recent mathematical models presented by Harrison and Hills (25). They extended the macroviscosity of the bulk solutions into the “micro” environment represented by the mass transfer coefficient. However, pH effects on diacetyl release, as they were recently shown (7, 26), were not reported. The present study distinguishes between two microregions, the free water phase exhibiting the same flavor diffusion coefficients as bulk water and the sucrose molecules including the associated water of hydration. This is in agreement with the depiction of Darling et al. (27) on the diffusion of small molecules in aqueous polymer solutions, which seems to be also reasonable for sucrose at concentrations up to 50% (w/v). Free water between the disaccharide molecules allows high mobility of the volatiles in liquids, resulting in dynamic flavor release

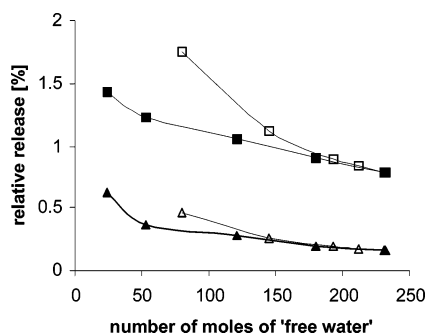


Figure 5. Correlation between the mole number of “free water” and predicted release of ethyl 2-methylbutyrate (■) and β -damascenone (▲) from sodium chloride solutions (open symbols) and sucrose solutions (solid symbols) using different approaches for the estimation of solute hydration.

independent from bulk solution viscosity, but dependent from the initial concentration built up in the nonassociated water phase (eqs 6 and 11) and, additionally, dipole interactions in the case of hydrophilic compounds (eq 13). The mass transfer coefficient given in eq 2 hence considers two types of kinematic viscosity, that is, the overall viscosity of the bulk solution (applied in eq 3), which increases with increasing solute concentration, and the viscosity of pure water (applied in eq 4).

Comparing the theoretical release data of a previous study on sodium chloride solutions with applied solute concentrations up to 100 g L^{-1} (10) and those of the present work, **Figure 5** exemplarily shows the correlation between free water volume calculated with different approaches (cf. ref 10) and relative release rates of hydrophilic ethyl 2-methylbutyrate and hydrophobic β -damascenone. The correlations show a good fit for β -damascenone, indicating that the free water volume was solely responsible for its changing release from both types of solution. Consequently, viscosity did not significantly affect flavor release, as the addition of sodium chloride to water insignificantly affected solution viscosity (data not shown). In the case of hydrophilic ethyl 2-methylbutyrate the corresponding curves are congruent only up to sucrose and sodium chloride concentrations of approximately 200 and 50 g L^{-1} , respectively. Higher sucrose concentrations led to comparably lower release rates with decreasing free water volume. Thus, sucrose at high concentrations seemed to have a stronger attractive power for hydrophilic flavors than sodium chloride, probably due to the drastically shrunken hydrophilic spheres enabling considerably intensified interactions (of which some may be of direct nature) between flavor dipoles and the hydroxyl groups of the sugar (cf. ref 23).

Sucrose/Sucrose Interactions Affect Molecular Motion in the Free Water and Flavor Release. **Table 6** compares the ratios between the experimentally determined absolute flavor amounts released from sodium chloride and sucrose solutions possessing solute concentrations of 100 and 500 g L^{-1} , respectively, with those from water. The ratio of these factors explains the differences between the two types of solutions with respect to their effect on absolute flavor release. Most of the flavors showed higher release from the sodium chloride solution than from the sucrose solution (ratio > 1), although the former possessed a larger volume of free water available for the solubilization of volatiles (**Figure 5**). In contrast to the experimental data the calculated release of hydrophobic compounds converges for both types of solutions with increasing solute concentrations (**Figure 5** and **Table 6**). **Table 6** hence indicates a decreasing effect of sucrose on flavor release not yet considered, respectively separated from that of flavor/sucrose interactions in the case of hydrophilic compounds, in the model.

Table 6. Comparison of Increasing Effects on Flavor Release from Water Due to the Addition of 100 g L^{-1} Sodium Chloride and 500 g L^{-1} Sucrose^a

flavor compound	ratio between flavor amounts released from solutions and from water		
	r_{NaCl}^b	r_{sucr}^c	$r_{\text{NaCl}}/r_{\text{sucr}}$
diacetyl	1.91	1.06	1.8
isobutyl acetate	1.97	0.75	2.6
ethyl 2-methylbutyrate	1.83	0.89	2.1
(Z)-3-hexenyl acetate	2.84	2.96	1.0
2,3-dimethylpyrazine	2.34	1.06	2.2
(Z)-3-hexenol	2.63	1.70	1.5
2-isobutylthiazole	2.86	1.84	1.6
furfuryl acetate	2.32	1.87	1.2
linalool	3.69	3.81	1.0
2-pentylpyridine	2.71	1.33	2.0
D-carvone	2.79	2.49	1.1
β -damascenone	2.67	1.69	1.6
γ -nonalactone	1.88	1.94	1.0

^a Factors represent the ratio between absolute flavor amounts dynamically released after 30 s from solutions and from water. ^b Calculated with experimental data adapted from ref 10. ^c Calculated with experimental data given in **Table 5**.

As the previous sucrose model considers flavor dipole/sucrose interactions and predicts release data parallel to those of experiments (**Figures 2** and **4**), the unknown effect must affect compounds of all polarities. The explanation for the above phenomenon was assumed to be found in the microregion of the solution. Increasing sucrose concentrations result in decreasing h_n (**Table 3**) and increasing solution viscosity and flavor release (**Figures 2** and **3**) and, at sucrose concentrations $> 40\%$, in sucrose/sucrose interactions (6, 21) and flavor/sucrose interactions (eq 13). All of the above effects were considered in the model with the exception of sucrose/sucrose interactions. Not only does the viscosity of the “continuous phase” or “continuous microregion” (hydrated sucrose molecules) increase upon addition of high amounts of sucrose to water, but flavors are also sterically hindered to move in the free water phase due to the decreased distances between hydrated sucrose molecules and sucrose oligomers caused by sucrose/sucrose interactions. As these structures are fluctuating and constantly changing, the velocity of volatiles movement in the capillaries of concentrated solutions is a random process, being another factor causing higher CV at high sucrose concentrations (**Table 5**). This hindrance does not occur in sodium chloride solutions (at least at concentrations up to 100 g L^{-1}), as there will be a regular, “crystal-like” orientation of hydrated Na^+ and Cl^- at high solute concentrations with ion–dipole interactions being the only effect on flavor release. To account for the effect in sucrose solutions, a factor b characterizing the sterical hindrance for each volatile to move in the solutions capillaries of free water has to be included in eq 4:

$$Sc = \mu b / (\rho D) \quad (14)$$

b is a function of sucrose concentration and depends on the molecular shape of the volatiles. For sucrose concentrations lower than $\sim 40\%$ b should equal 1, whereas at higher concentrations it takes a value > 1 , minimizing flavor diffusion in the solution (cf. eqs 4 and 14). Due to the limited sucrose concentrations applied in the study, the presented experimental data are not suitable for the determination of b . However, food liquids normally contain sucrose in concentrations $\ll 40\%$, and the model eq 11 considering eq 13 was shown to sufficiently predict flavor release from solutions of such concentrations. The above assumption might explain the results of Roberts et al.

(15). They used very high sucrose concentrations in their experiments: 519 and 689 g kg⁻¹, which were higher than those applied in this study (≤ 500 g L⁻¹), and found increasing viscosity when comparing the two solutions. Sterical hindrance for the volatiles of different polarity to move in the solution may have governed their “immobilization”, resulting in decreased flavor release rates. This process is comparable to that in collapsed phases with their dense matrix encapsulating the volatiles causing a considerable slowing of molecular diffusion (28). Adsorption effects proposed by the group are also in accordance with the present assumptions, as drastic depletion of water of hydration enables the formation of hydrogen bonds between hydroxyl groups of the sugars and polar functions of volatile compounds (23). Consistently, recent results showed binding of volatiles to guar gum as well as the corresponding viscosity not to be of significant importance for the initial dynamic release process from thickened emulsions (9): Already small amounts of guar gum led to a considerable increase of emulsion viscosity. Sterical hindrance, however, and flavor dipole/solute interactions should not have had any influence due to the sufficient space between the hydrated polymers (cf. ref 27) and their voluminous hydration shells, respectively.

The experimental results obtained under simulated mouth conditions (3) using very low flavor concentrations confirmed the model theory that binding of water by sucrose is rate limiting for initial dynamic flavor release. Volatile release was independent of sucrose solution viscosity but dependent on free water volume and solute/volatile (hydrophilic) interactions, similar to the release process from sodium chloride solutions (10), and, at high sucrose concentrations, from steric hindrance. In accordance with Richardson et al. (21) and Starzak et al. (6) results showed a critical sucrose concentration of ~40%, which had a different impact on the mobility and, therefore, release of polar and nonpolar flavors, respectively (Figures 2 and 4). The overall effect of sucrose on flavor release was small compared, for example, to the effect of oil in emulsions (8). Nevertheless, small differences of release are assumed to be of sensory importance, if the individual threshold for a certain flavor is exceeded. A considerable synergy between the sugar/sweetener content of a food and flavor perception was made evident by recent authors (1, 2). A major challenge of future flavor research will be to build the bridge between real-time concentration data of volatile and nonvolatile flavors, such as sucrose, and human flavor perception.

ABBREVIATIONS USED

PG, propylene glycole; ANOVA, analysis of variance; LSD test, Fisher's least significant difference 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 (m²); V_{hs} , volume of the headspace (m³); Re, Reynold's number; Sc, Schmidt's number; P , volatile permeability (m² 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 bulk phase (kg m⁻³); μ , dynamic viscosity of the bulk phase (kg m⁻¹ s⁻¹); D , diffusivity (m² s⁻¹); δ , effective film thickness of flowing air in contact with the bulk phase (m); V_f , volumetric flow rate of air (m³ s⁻¹); p , vapor pressure (Pa); S , aqueous solubility (kg m⁻³); $c_{0,sucr}$, initial flavor concentration in the nonbound water phase; a , factor; $n_{w,t}$, number of moles of total water; $n_{w,b}$, number of moles of bound water; V_{re} , volume of the reactor (m³); m_{sucr} , total mass of sucrose in solution (kg); n_{sucr} , number of moles of sucrose; h_n , hydration number; S_{NaCl} , aqueous solubility of

flavors in sodium chloride solutions (kg m⁻³); f_i , ratio; z , exponent; S_{sucr} , aqueous solubility of flavors in sucrose solutions (kg m⁻³); CV, coefficient of variation (%); b , factor.

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