

Modeling Flavor Release from Aqueous Sucrose Solutions, Using Mass Transfer and Partition Coefficients

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The penetration theory of interfacial mass transfer was used to model flavor release from aqueous solutions containing different concentrations of sucrose. The mass transfer coefficient and the gas/solution partition coefficient are the main factors of the model influencing the release in time. Parameters governing the isolation by a purge and trap method at mouth conditions (volume, temperature, and artificial saliva) were used in the model description of the flavor release. Viscosities of the different sucrose solutions (0–60 w/v %) at 37 °C were estimated, and their influence on the mass transfer coefficients was determined. The gas/solution partition coefficients for ethyl acetate, methyl butanoate, ethyl butanoate, hexanal, and octanal were measured for the different sucrose concentrations at 37 °C. At lower sucrose concentrations the partition coefficient primarily controls flavor release during a purge time of 10 min, whereas at higher sucrose concentrations the influence of the mass transfer coefficient is more important.

Keywords: Flavor release; interfacial mass transfer coefficient; partition coefficient; sucrose; orange aroma

INTRODUCTION

The instrumental analysis of the release of volatile compounds from solutions containing sucrose and an orange aroma formed part of the study of sweetness–flavor interactions in models for soft drinks (Nahon et al., 1998). In the presence of sucrose, volatile compounds from an orange aroma (a watery vapor phase of stripped orange juice) were isolated by a purge and trap method at mouth conditions (volume, temperature, and artificial saliva), during 10 min. The volatile compounds were trapped onto an adsorbance material (Tenax) and then quantified by gas chromatography coupled with flame ionization detection (GC-FID). To understand the effect of the addition of sucrose (as compared with an addition of, e.g., sodium cyclamate), the release of volatile compounds was studied in solutions containing increasing concentrations of sucrose. The latter caused an increased release of the volatile compounds with short GC-FID retention times and a decreased release of the volatile compounds with longer retention times (Nahon et al., 1998). Modeling of these results will improve the understanding of the system worked with and elucidate the parameters influencing the flavor release.

Harrison and Hills (1997) modeled the dynamic flavor release from liquid emulsions in the mouth. Their model revealed the most important parameters influencing the release. One important parameter is the viscosity, which determines the diffusion coefficient, D , and thus the

interfacial mass transfer coefficient, h_d (Harrison et al., 1997). The mass transfer coefficient is a measure for the rate of release (De Roos and Wolswinkel, 1994). The other important parameter is the gas/solution partition coefficient, K_{gs} , which is influenced by the sucrose concentration as well and reflects the concentration ratios at equilibrium (De Roos and Wolswinkel, 1994).

In the literature, several tables can be found reporting the viscosities for different sucrose solutions, at different temperatures [e.g., Bates (1942)]. However, these tables do not give the exact viscosity values for the sucrose concentrations relevant to the present study and, moreover, not for the specific temperature of 37 °C. Bretsznajder (1971) and Génotelle (1978) presented equations and figures reflecting relationships between temperatures and viscosities for various sucrose solutions.

Table 1 shows an overview of the authors reporting partition coefficients for five volatile compounds studied in the present experiment. These volatile compounds were taken from the three retention time groups as distinguished by Nahon et al. (1998): ethyl acetate and methyl butanoate (short GC-FID retention times), ethyl butanoate and hexanal (medium retention times), and octanal (long retention times). Several gas/solution partition coefficients were reported in the literature, but not for all sucrose solutions and at temperatures different from 37 °C. Kieckbusch and King (1979a), Hall and Andersson (1983), and Overbosch et al. (1991) indicated that the partition coefficients increase with increasing temperatures. Hall and Andersson (1983) found that varying the temperature changes not only the overall concentration level of volatile compounds in the gas phase but also the relative composition of the gas phase.

In the present study, the dependency of the mass transfer coefficient on the viscosity is described in an

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Table 1. Reported Partition Coefficients ($\times 10^3$) for Ethyl Acetate, Methyl Butanoate, Ethyl Butanoate, Hexanal, and/or Octanal

A. Specifications of the Determinations; Author Number, Author, Volatile Concentration, Temperature, Equilibration Time, and Method					
no.	author	volatile concn (ppm)	temp ($^{\circ}$ C)	equilibration time (min)	method
1	Amoore and Buttery (1978)	solubility level	25		calculation
2	Buttery et al. (1965)	5	25	15	SHGC
3	Buttery et al. (1969)	5–200	25	>30	SHGC
4	De Roos and Wolswinkel (1994)		37	60	stripping
5	Guitart et al. (1989)	20–5000	37	30	SHGC
6	Hall and Andersson (1983)	0.25–1.2	40	60	SHGC
7	Kieckbusch and King (1979b)	400	30	<30	SHGC
8	Kolb et al. (1992)	± 1000	37	60	extrapolated/calculated
9	Landy et al. (1995)	20–1000	25		exp dilution mol fractions
10	Voilley and Bosset (1986)	1000/10000	25	5	SHGC

B. Partition Coefficients Determined in Water and Sucrose/Glucose Solutions; Author Number in Parentheses					
	ethyl acetate	methyl butanoate	ethyl butanoate	hexanal	octanal
water	9.2 (7)	8.4 (3)	22.4 (9)	6.9 (2)	5.4 (2)
	9.0 (5)	11.0 (1)		8.7 (3)	14.0 (1)
	9.6 (9)	15.8 (4)		11.4 (1)	21.0 (3)
	11.6 (10)			36 (6)	79 (6)
	14.8 (8)				
+ sucrose	12.0–30.3 (7)	<15.8 (4)			
+ glucose	38.1 (10)				

equation. The gas/solution partition coefficients for ethyl acetate, methyl butanoate, ethyl butanoate, hexanal, and octanal over the different sucrose solutions were determined. Then the release of these volatile compounds from sucrose solutions was described by a model. The mass transfer coefficient in water was used as a fitting parameter to approach experimental results published before (Nahon et al., 1998). Modeling these experimental results will reveal the parameters influencing the flavor release.

MATERIALS AND METHODS

Sample Preparation. Samples were solutions of sucrose (CSM Suiker BV, Amsterdam, The Netherlands) and volatile compounds in demineralized water. The sucrose concentrations were 0, 5, 10, 20, 40, and 60 w/v %. The volatile compounds were ethyl acetate (E. Merck, Darmstadt, Germany), ethyl butanoate (Janssen Chimica, Geel, Belgium), methyl butanoate, hexanal, and octanal (all Merck-Schuchardt, Germany). The purities of the volatile compounds were all >98% (synthesis-grade). Preparation of solutions was at room temperature (22 $^{\circ}$ C), 6–15 h before analysis at 37 $^{\circ}$ C.

Viscosity. The required viscosities at 37 $^{\circ}$ C were calculated by using equations given in the literature. Génételle (1978) established the following relationship among the dynamic viscosity (η), the sucrose concentration, and the temperature of the solution

$$\log \eta = 22.46N - 0.114 + \Phi(1.1 + 43.1N^{1.25}) \quad (1)$$

in which $N = (B/(1900 - 18B))$ is the molar fraction of sucrose, B being $^{\circ}$ Brix, and $\Phi = (30 - T)/(91 + T)$, T being temperature. The data generated with the help of eq 1 deviate maximally 1% from the data for standard solutions as published by the National Bureau of Standards (Bates, 1942). Given the experimental temperature of 37 $^{\circ}$ C, the weight fractions or $^{\circ}$ Brix for the sucrose solutions were determined to be able to calculate the viscosities for the different sucrose solutions with the help of eq 1. An Abbe refractometer (Atago type no. 302 with Power Source, Atago, Japan) was used for this determination.

Gas/Solution Partition Coefficients. The samples for the measurements of the gas/solution partition coefficients were prepared by adding 14–17 ppm of volatile compound to the various sucrose solutions. Sealed volumetric flasks with solu-

tions containing ethyl butanoate, hexanal, or octanal were placed in a sonification bath (Sonicator Ultrawave CE, Fa Ultrawave Limited, Cardiff, U.K.) at room temperature for 30 min, to fully solubilize these more apolar volatile compounds. The homogeneity of the solutions was checked visually, according to the method described by Buttery et al. (1969).

The equilibrium concentrations of the volatile compounds in the gas phase were measured at 37 $^{\circ}$ C using static headspace gas chromatography (SHGC). The sample solution (3 mL) was transferred into a 12 mL vial, which was capped and incubated at 37 $^{\circ}$ C for 15 or 30 min in the headspace unit (Fisons HS800, Fisons Instruments, Weesp, The Netherlands) of the gas chromatograph. The gas/solution equilibrium is considered to be reached when the volatile concentration in the headspace remains constant. For ethyl acetate and octanal an incubation time of 15 min was testified to be sufficient; for methyl butanoate, ethyl butanoate, and hexanal an equilibrium was reached after an incubation time of 30 min. After incubation, 300 μ L of the sample headspace passed an MFA 815 cold trap (Fisons Instruments) for cryofocusing and was then injected into an HRGC 5300 Mega series gas chromatograph (Carlo Erba Instruments, Interscience BV, Breda, The Netherlands). The GC was equipped with a DB-Wax column (30 m \times 0.542 mm \times 1.0 μ m) and a flame ionization detector at 220 $^{\circ}$ C. The oven temperature was 40 $^{\circ}$ C for 5 min and then programmed to 110 $^{\circ}$ C at a rate of 3 $^{\circ}$ C/min and further to 170 $^{\circ}$ C at 20 $^{\circ}$ C/min. One measurement consisted of at least three repetitions of this method.

For calibration curves, 2 or 10 μ L of a pure volatile compound was dissolved in 10 mL of solvent, and different volumes of these two solutions were manually injected on the column. The solvent used for ethyl acetate and methyl butanoate was demineralized water, and the solvent for ethyl butanoate, hexanal, and octanal was hexane. The method was repeated two times, to obtain significant and reliable calibration curves ($R^2 > 0.84$).

The gas/solution partition coefficient K_{gs} is given by the equation

$$K_{gs} = C_g^{eq} / C_s^{eq} \quad (2)$$

in which C_g^{eq} is the concentration of the volatile compound in the gas phase at equilibrium, and C_s^{eq} is the concentration of the volatile compound in the solution at equilibrium. As the volatile compound in the system distributes between the gas phase and the solution until equilibrium has been reached,

the concentration in the solution can be calculated from the initial volatile concentration, the concentration in the gas phase, and the volumes of the gas phase and solution

$$C_s = C_s(0) - C_s(v_g/v_s) \quad (3)$$

in which $C_s(0)$ is the initial volatile concentration in the solution and v_g and v_s are the volumes of the gas phase and the solution, respectively.

Flavor Release Model. Parameters in the model of Harrison and Hills (1997) were adjusted to approximate the experimental design used in the study of Nahon et al. (1998). The ratios of release in time are then given by the model

$$\frac{C_g(t)}{C_s(t)} = \frac{A_{gs}h_d}{v_g} \left[\frac{\exp r_1 t - \exp r_2 t}{r_1 - r_2} \right] \quad (4)$$

in which r_1 , $r_2 = f(h_d, K_{gs}, Q, A_{gs}, v_g, v_s)$. Apparently, the concentration of the volatile compound in the headspace in time, $C_g(t)$, is a function of the initial concentrations in the solution, $C_s(0)$, the viscosity-dependent mass transfer coefficient, h_d , the gas/solution partition coefficient, K_{gs} , the nitrogen gas flow rate, Q , the interface surface area, A_{gs} , the volume of the headspace, v_g , and the volume of the solution, v_s (sample plus artificial saliva).

Parameters were substituted in the model presented by eq 4. Similar to the expressions reported by Harrison and Hills (1997), r_1 and r_2 in eq 4 are given by

$$r_1 = -\frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4\beta}}{2} \quad (5)$$

and

$$r_2 = -\frac{\alpha}{2} - \frac{\sqrt{\alpha^2 - 4\beta}}{2} \quad (6)$$

with

$$\alpha = \frac{Q}{v_g} + \frac{h_d A_{gs}}{v_g K_{gs}} + \frac{h_d A_{gs}}{v_s} \quad (7)$$

and

$$\beta = Q h_d A_{gs} / v_g v_s \quad (8)$$

The following parameters, necessary for eqs 4–8, were known from the setup of the release experiments: $Q = 20$ mL/min; $v_g = 31$ mL; and $v_s = 19$ mL.

The partition coefficients, K_{gs} , were determined for the different volatile compounds, dissolved in the different sucrose solutions. As the volatile concentrations in and above the solutions (C_s and C_g) are unknown, the relative concentrations given by $C_g(t)/C_s(0)$ will be studied in time.

The mass transfer coefficient, h_d , is an unknown parameter, which can be described as a function of the viscosity, η . Harrison et al. (1997) and Bakker et al. (1998) reported the following relationship:

$$h_d \propto 1/\sqrt{\eta} \quad (9)$$

Starting from this relationship, the mass transfer coefficient can be described as a function of the mass transfer coefficient in water, $h_d(0)$, the viscosity in water, $\eta(0)$, and the viscosity for a specific sucrose solution with concentration C_{suc} .

$$\frac{h_d(C_{suc})}{h_d(0)} = \sqrt{\frac{\eta(0)}{\eta(C_{suc})}} \quad (10)$$

As $\eta(0)$ and $\eta(C_{suc})$ will be calculated using eq 1, the mass transfer coefficient for a specific volatile compound at a given sucrose concentration depends on $h_d(0)$ for that volatile

Table 2. Average and Standard Deviations ($n = 10$ for 0 and 60 w/v % Sucrose; $n = 3$ for 5, 10, 20, and 40 w/v % Sucrose) for Gas/Solution Partition Coefficients ($\times 10^3$) of Ethyl Acetate, Methyl Butanoate, Ethyl Butanoate, Hexanal, and Octanal for Different Sucrose Solutions (w/v %) at 37 °C (Verset, 1998)

sucrose (w/v %)	ethyl acetate	methyl butanoate	ethyl butanoate	hexanal	octanal
0	10.3 ± 0.33	11.2 ± 0.35	14.8 ± 0.67	12.9 ± 0.99	21.1 ± 1.80
5	11.2 ± 0.26	13.8 ± 0.37	18.9 ± 0.59	13.0 ± 0.08	20.0 ± 0.32
10	11.3 ± 0.61	14.9 ± 0.12	19.7 ± 0.50	13.5 ± 0.04	19.2 ± 0.38
20	13.2 ± 0.78	16.6 ± 0.65	22.1 ± 1.98	13.3 ± 0.10	17.5 ± 0.99
40	16.4 ± 0.74	21.0 ± 0.08	28.2 ± 1.18	13.9 ± 0.15	16.1 ± 1.49
60	22.8 ± 1.66	28.4 ± 7.76	29.8 ± 1.72	13.1 ± 1.09	14.3 ± 3.17

Table 3. Weight Fractions/°Brix (w/w %) and Dynamic Viscosities η (cP; Calculated from Equation 1) for Different Sucrose Solutions (w/v %) at 37 °C (Génotelle, 1978)

sucrose (w/v %)	sucrose (w/w %)	viscosity (cP)	sucrose (w/v %)	sucrose (w/w %)	viscosity (cP)
0	0	0.67	20	18.25	1.20
5	4.50	0.76	40	34.50	2.55
10	9.25	0.88	60	48.75	6.99

compound. The interface area, A_{gs} , concerns the complete interface between the gas phase and the solution, including the gas bubbles in the solution caused by the nitrogen flow. As A_{gs} can only be approximated, it was included in the mass transfer coefficient to give hda ($= h_d \times A_{gs}$). Then hda depends on the sucrose concentration and the magnitude of $h_d(0)$. The latter was used as the fitting parameter to approach the experimental results with the model description (eq 4).

Using a partition coefficient measured for a certain volatile compound in a sucrose solution (Table 2), and given the relationship between the mass transfer coefficient and the sucrose concentration, the release of this volatile compound in time can be determined with the use of eq 4. To be able to compare this predicted release with that determined previously (Nahon et al., 1998), the time–release curves were integrated with the help of the technical computing program Mathematica (version 3.0, Wolfram Research Inc., Champaign, IL). For each volatile compound, the amount of volatile released from the sucrose solution in 10 min (i.e., the purge time) was related to the amount of volatile released from water. These ratios of release predicted by the model (integration areas) were compared with the ratios of release obtained in the purge and trap experiment (GC-FID peak areas). The $h_d(0)$ was used to adjust the ratios of release predicted by the model. The optimal $hda(0)$ was given by the optimal least-squares solution for the fit of the model integration ratios to the experimental peak area ratios.

RESULTS AND DISCUSSION

Viscosity. The weight fractions or °Brix for the different sucrose solutions and the calculated viscosities are given in Table 3. These viscosities are in the same range as values reported in the literature (Bates, 1942; Nawar, 1971; Voilley and Bosset, 1986) when considering the different sucrose concentrations and the different temperatures. The °Brix was determined at room temperature and then used for the calculation of the viscosity at 37 °C. This temperature difference introduces a deviation in °Brix of ~0.5%, resulting in a deviation of maximally 2.5% for the calculated viscosity according to Génotelle (1978).

Richardson et al. (1987) studied the mobility of water in sucrose solutions. They distinguished several regions. In the first region, sucrose concentrations varying from 0 to 40 w/w %, water mobility decreases linearly. The second concentration range of 40–60 w/w % sucrose shows a nonlinear decreasing water mobility, due to the

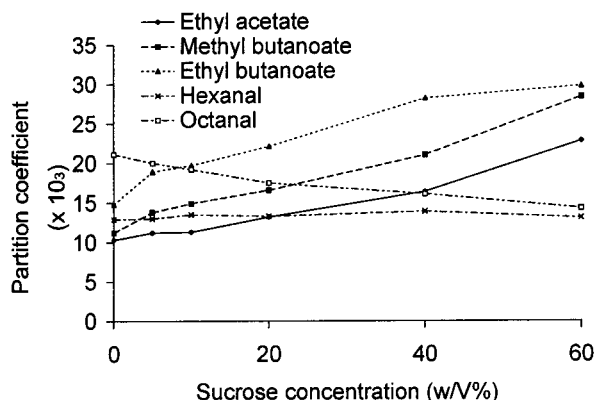


Figure 1. Partition coefficients ($\times 10^3$) of ethyl acetate, methyl butanoate, ethyl butanoate, hexanal, and octanal as a function of the sucrose concentration (w/v %).

formation of a network by intermolecular hydrogen bonds between water and sucrose, hydrogen bond bridging of water between sucrose molecules, and sucrose–sucrose hydrogen bonding. The calculated viscosities (eq 1) show a nearly linear increase up to a concentration of 20 w/w % and next a nonlinear increase (compare Table 3).

Gas/Solution Partition Coefficients. Figure 1 shows the gas/solution partition coefficients for the five volatile compounds as a function of the sucrose concentration in the solutions. Apart from ethyl butanoate, the evolution of these partition coefficients shows a grouping of volatile compounds that is similar to the division in retention time groups made in the results of the instrumental analysis reported before (Nahon et al., 1998).

In the present experiment, we choose specific volatile concentrations (14–17 ppm) for measuring the partition coefficients over the different sucrose solutions. Buttery et al. (1969) stated for hexanal that the partition coefficient was constant up to its point of saturation, at 5000 ppm. Land (1978) also clarified in his paper that the gas/solution partition coefficient is constant up to the saturated vapor pressure at the solubility limit. The equilibration time used for the determination of the gas/solution partition coefficients varied often from 15 to 30 min [e.g., Buttery et al. (1965, 1969), Chaintreau et al. (1995), and Chai and Zhu (1998)]. An exception was the equilibration time chosen by Voilley and Bosset (1986), which was set at 5 min. Whereas the model describes the release of a single volatile compound, the release in the purge and trap system concerned a mixture of orange aroma compounds. Guitart et al. (1989) indicated that the composition of the mixture has very little influence on the partition of its constituents. Chaintreau et al. (1995) proved that the influence of other volatiles in a model mixture of flavors on the individual component concentrations in the gas phase was not noticeable. However, Bohnenstengel et al. (1993) investigated the influence of interactions between substances on the SHGC. They found that even small changes in the sample composition can cause changes in the resulting headspace composition. The determination of the partition coefficients of volatiles in the presence of other volatile compounds can therefore still be of interest for study.

The authors mentioned in Table 1 determined partition coefficients that were in the same range as those determined in the present experiment, especially when

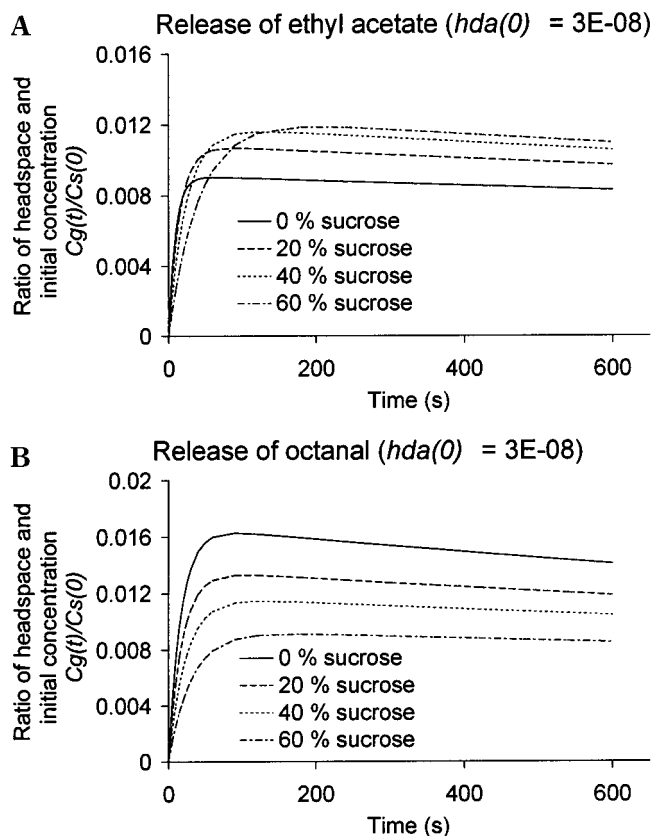


Figure 2. Predicted release (eq 4) of (A) ethyl acetate and (B) octanal into headspace from solutions containing sucrose (0, 20, 40, and 60 w/v %) and an orange aroma, represented by the ratio of headspace and initial concentration of the volatile compound as a function of time. $hda(0)$ was set at $3 \times 10^{-8} \text{ m}^3/\text{s}$ for both compounds.

considering the temperature used for the determination (compare Tables 1 and 2). Amoore and Buttery (1978), Overbosch et al. (1991), and Landy et al. (1995) reported that the partition coefficient increases with the carbon chain length for esters and aldehydes.

Flavor Release Model. The release of ethyl acetate from solutions containing sucrose and an orange aroma increases with increasing sucrose concentrations as predicted by eq 4 (Figure 2A). For octanal, the release decreases with increasing sucrose concentrations (Figure 2B). Increasing the sucrose concentration makes the solvent character of a solution more hydrophobic, which explains the increased and decreased partition coefficients for ethyl acetate and octanal, respectively. The maximal ratio of headspace and initial concentration reflects the evolution of the partition coefficients. As the partition coefficient in water is smaller for ethyl acetate than for octanal, its maximal release ratio is smaller. At 40 w/v % sucrose, the partition coefficients of ethyl acetate and octanal are equal (Figure 1 and Table 2), resulting in an equal maximal release ratio for a 40 w/v % sucrose solution (compare panels A and B of Figure 3).

The mass transfer coefficient decreases with increasing sucrose concentrations. In Figure 3A,B this is indicated by a smaller initial slope of the time–release curve (Bakker et al., 1998). These authors also reported that the initial release rates for diacetyl decreased as the concentration of gelatin increased, that is, as the viscosity increases. Chandrasekaran and King (1972) found that the activity coefficients for ethyl acetate and

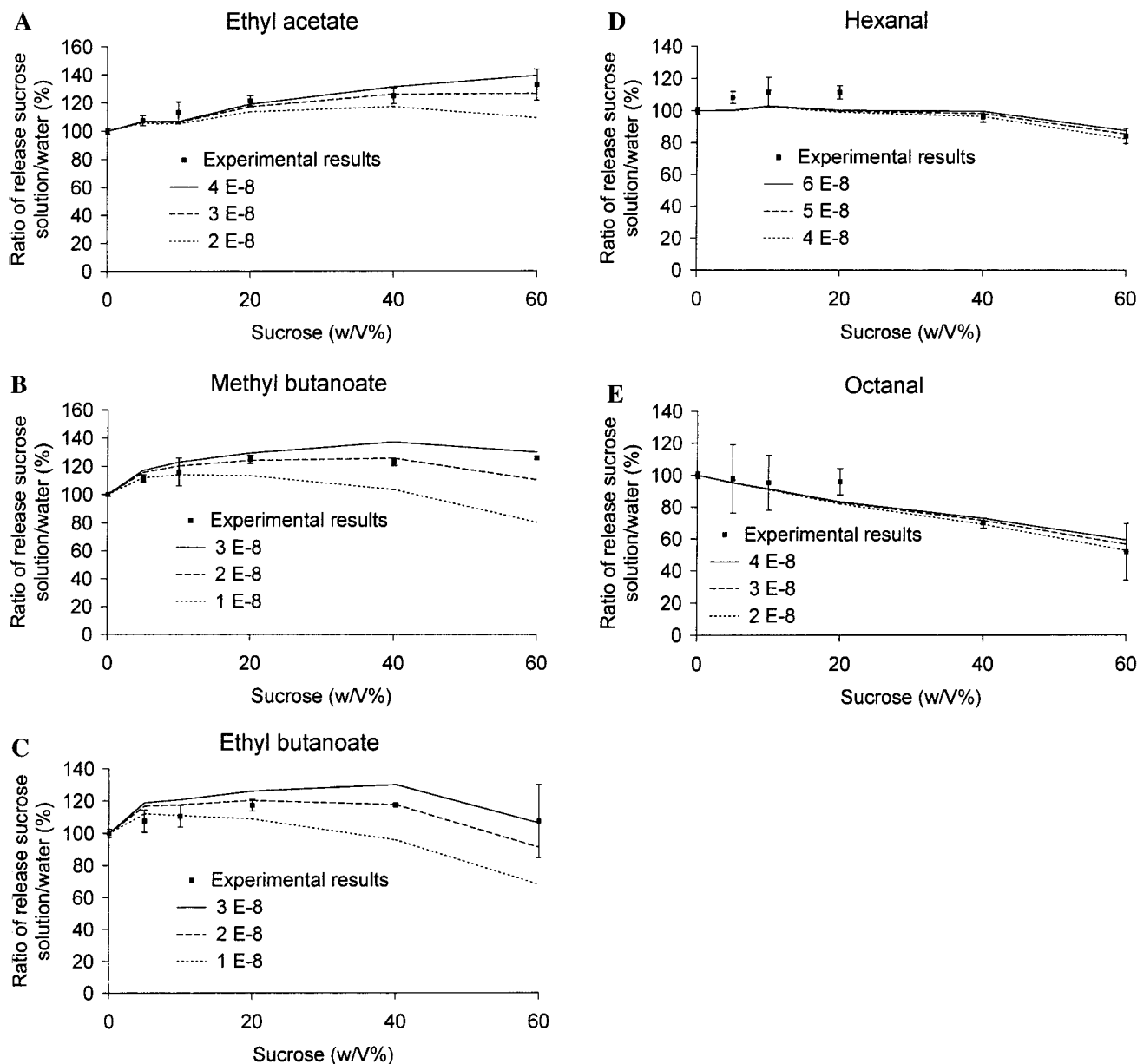


Figure 3. Peak area and integration ratios representing the release of (A) ethyl acetate, (B) methyl butanoate, (C) ethyl butanoate, (D) hexanal, and (E) octanal, for different sucrose concentrations. The peak area ratios (■) and their standard deviations were deduced from experimental observations (Nahon et al., 1998); the integration ratios were obtained by modeling (eq 4). The model predictions are given for three $hda(0)$'s, the middle providing the optimal fit.

hexanal increased with increasing sugar concentrations. The diffusion coefficients of these volatile compounds decreased with increasing sucrose concentrations. Darling et al. (1986) observed for isopentyl acetate that for higher sucrose concentrations (> 30%) the viscosity of the solution increased steeply and, consequently, the diffusion coefficient fell.

To compare the release described by the model (eq 4) with the release in the purge and trap system, the areas under the release curves were integrated. In Figure 3 the integration ratios as obtained with the model (lines) and the peak area ratios as obtained in the experiments (symbols) (Nahon et al., 1998) are compared. For each volatile compound, the model predictions for three $hda(0)$'s are given, the middle $hda(0)$ being the optimal least-squares solution for the fit of the model to the experimental results. The optimal values of $hda(0)$ for ethyl acetate, methyl butanoate, ethyl butanoate, hexanal, and octanal were 3×10^{-8} , 2×10^{-8} , 2×10^{-8} , $5 \times$

10^{-8} , and 3×10^{-8} m^3/s , respectively. Figure 3 reflects the fit of the model to the experimental results. Figure 3A shows that the predicted and observed release of ethyl acetate increases with increasing sucrose concentration. Choosing a higher mass transfer coefficient (and thus hda) increases the release for all volatile compounds (Figure 3). Comparing panels A–C with D and E of Figure 3 shows that the influence of the mass transfer coefficient/ hda is much smaller for the volatile compounds hexanal and octanal. Increasing the sucrose concentration, and thus the mass transfer coefficient, hardly influences the ratios of release for these compounds. Therefore, changes in the fitting parameter hda will not influence these ratios either. The optimal values of $hda(0)$ for the five volatile compounds are similar. Overall they vary from 2×10^{-8} to 5×10^{-8} m^3/s . There is no special trend when more polar or more apolar volatile compounds are considered. The purge and trap method used for the instrumental analysis of the flavor

release included stirring of the solution. Bakker et al. (1998) reported an effect of stirring rate on the dynamic release of diacetyl. Therefore, stirring is one of the factors introducing variation in the experimental data. As the fit of the model to the experiments is adjusted per volatile compound, the fitting parameter hda will vary as well. According to Overbosch et al. (1991), the diffusion coefficient does not vary significantly among flavor compounds. As the diffusion coefficient determines the mass transfer coefficient, this latter coefficient will not vary much with the flavor compound either. De Roos and Wolswinkel (1994) also neglected differences in diffusion coefficients among volatile compounds in their release study. However, Harrison and Hills (1997) stated that the $h_d(0)$ will vary among volatile compounds.

If the hda giving the best fit of the model to the experimental results is known, the expected mass transfer coefficient h_d can be deduced from an approximation of the interface surface area A_{gs} . This area is composed of the surface area of the solution and the surface areas of the nitrogen gas bubbles purged through the solution. The diameter of the tube through which the nitrogen gas is let into the solution is 3×10^{-3} m, which produces bubbles with a calculated volume of 1.4×10^{-8} m³. Given the experimental nitrogen flow of 20 mL/min, 14147 bubbles will pass through the solution during the 10 min of the analysis. This gives an interface area of 0.4 m² as provided by the bubbles. The surface area of the solution can be assumed to be negligible ($\cong 4.8 \times 10^{-4}$ m²). As the average best fitting hda was 3×10^{-8} m³/s in the present experiment, the best estimate of the mass transfer coefficient in this system is 7.5×10^{-8} m/s.

When the model predictions (Figure 3) are compared with the evolution of the partition coefficients (Figure 1), it appears that the ratio curves at low sucrose concentrations are mainly controlled by the partition coefficient of a specific volatile compound. When the sucrose concentration and thus the viscosity of the solution increase, the mass transfer coefficient becomes smaller (as given by eq 10). Then the partition coefficient loses impact on the release during a purge time of 10 min. In accordance with the explanations of Richardson et al. (1987), the viscosity of the solutions increases, especially for the two highest sucrose concentrations (40 and 60 w/v %) in Table 3. A comparison of Figures 2 and 3 demonstrates that the partition coefficient has the largest influence on the ratios of release up to a sucrose concentration of 40 w/v %. De Roos and Wolswinkel (1994) also found that the effect of the resistance to mass transfer on the relative release rate was relatively small and that flavor release was mainly partition-controlled for water and an aqueous solution of 25% sucrose.

The model describing the flavor release from the sucrose solutions includes the mass transfer coefficient as being dependent on the viscosity. It is questionable whether it is actually the viscosity or the sucrose concentration influencing the diffusion coefficient and thus the mass transfer coefficient. Roberts et al. (1996) studied flavor release for different thickeners at equal viscosities and found that the three thickened systems did not have the same flavor release profiles. Thickener-specific influence on the flavor release was revealed. Apparently, viscosity-dependent mass transfer does occur, but other mechanisms such as changes in the

water activity are also important. Darling et al. (1986) explained that interactions between long-chain polymers will induce the "macro" viscosity of solutions, although still very large pores of "free" water are available to small molecules for diffusion. Diffusion in this water phase is not related to the viscosity of the bulk solution. For solutions thickened by large quantities of small molecules (e.g., sucrose) the macro viscosity extends into the "micro" environment, which will be experienced by the diffusing aroma molecules. Richardson et al. (1987) reported a decreasing water mobility when the sucrose concentration passes 40 w/w %. In this study, the mass transfer coefficient could be better described as a function of the sucrose concentration instead of the viscosity.

In conclusion, the model described the dynamic flavor release for five volatile compounds from aqueous sucrose solutions. By determination of the viscosities and the partition coefficients, the model provided an acceptable fit to the experimental data obtained with instrumental analysis. The model description revealed that at low sucrose concentrations the partition coefficient primarily controls the flavor release, whereas at higher sucrose concentrations the mass transfer coefficient has more influence.

ABBREVIATIONS USED

A_{gs} , interface surface area; B , °Brix; C_g , concentration of volatile compound in gas phase; C_s , concentration of volatile compound in solution; C_{suc} , concentration of sucrose; D , diffusion coefficient; eq, equilibrium; FID, flame ionization detection; g, gas phase; GC, gas chromatography; h_d , mass transfer coefficient; hda , $h_d \times A_{gs}$; K_{gs} , gas/solution partition coefficient; N , molar fraction of sucrose; η , dynamic viscosity; Q , gas flow rate; s, solution; SHGC, static headspace gas chromatography; t , temperature; v_g , volume of the headspace; v_s , volume of the solution.

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