Effect of Breathing and Saliva Flow on Flavor Release from Liquid Foods

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Using the penetration theory of interfacial mass transfer, mathematical models have been developed to describe flavor release from liquid foods in the mouth, which incorporates the effects of breathing and saliva dilution. It has been assumed that the rate-limiting step for flavor release is resistance to mass transfer across the liquid−gas interface. This model has been applied to two types of liquid foods: first, aqueous solutions containing aroma-binding macromolecules and, second, liquid oil-in-water emulsions. The initial rates of release were found to be independent of both the rate of saliva production and gas flow rates due to breathing. However, at slightly longer times the saliva flow rate greatly influenced the quantity of flavor available for perception in the headspace.

Keywords: *Interfacial mass transfer; penetration theory; saliva; partitioning; headspace*

INTRODUCTION

Flavor is the primary factor determining consumer choice of food products. To produce a response, flavor compounds must be present in a concentration above a certain threshold and free to interact with receptors. The overall perception of flavor is generally understood to be a combination of both nonvolatile compounds in the saliva (taste) and volatile compounds transported to the olfactory epithelium (aroma). Flavorists are therefore eager to understand mechanisms of release and the interactions between ingredients and flavor in order to aid them in the development of new products. Although the flavor is generally understood to be the perception of both volatile and nonvolatile compounds while eating, we considered it, for our purposes, as indicating volatile aroma compounds only.

Although liquid foods are consumed almost immediately (typically within 2−3 s of ingestion) a proportion of the flavor-enriched liquid remains in the mouth as a thin film coating the oral cavity. The thickness of this coating, and hence the quantity of flavor residing in the mouth, will depend on the viscosity of the film. Further dilution of the remaining food−saliva mixture may alter the relative release rates of the volatiles and hence the aftertaste. Breath-by-breath mass spectrometry has shown that some volatiles persist in the nose-space long after the food has been swallowed (Taylor, 1996).

Release rates of volatiles from liquid foods, both directly after consumption and after swallowing, will depend on how the volatiles interact with other components of the food during dilution. The majority of flavors are hydrophobic and therefore preferentially partition into the lipid phase and not into the aqueous or gas phases (Buttery et al., 1973). Dilution of an oil-in-water emulsion system with saliva will therefore shift the aroma partitioning and change the release kinetics. In addition, macromolecules, such as proteins and polysaccharides, are known to bind flavor compounds either reversibly or irreversibly (Solms, 1986; Kinsella,

1989). Diluting the macromolecular concentration with saliva will therefore also shift the binding equilibrium and change the aroma release kinetics.

Interactions between food ingredients and flavor compounds have been studied, in the main, by measuring the release of volatiles from stirred liquid bulk phases into a headspace. To elucidate the primary factors governing flavor release from such systems mathematical models have been developed. These studies have established a number of important points. First, the rate-limiting step for flavor release is usually the transport of volatiles across the liquid/gas interface, which can be adequately described by the penetration theory of mass transfer (Harrison et al., 1997; Bakker et al., 1998). Second, increasing the viscosity of the liquid-phase reduces the rate of flavor release into the headspace (Bakker et al., 1998). Third, diffusion of flavor compounds between the lipid and aqueous phases of an emulsion is extremely fast compared to release across the gas−emulsion interface (Harrison et al., 1997). And finally, disassociation between the bound and unbound state of an aroma−macromolecule complex is extremely fast and therefore not rate limiting (Harrison and Hills, 1997b).

In a more dynamic system such as the mouth, where breathing and saliva dilution are present, the exchange between the bound and unbound state may not always be at equilibrium. Furthermore, if an emulsion is present in the mouth, saliva dilution will disturb the equilibrium partitioning between the aqueous and lipid phases and will further influence the rate of release. In this paper we focus on the effect of breathing and saliva dilution on the rate of flavor release from liquid oil-in-water emulsions and mixtures containing aroma-binding macromolecules.

THEORY OF FLAVOR RELEASE FROM LIQUIDS CONTAINING MACROMOLECULES

Theory. In a previous paper we presented a mathematical model which described the release of volatiles into a closed headspace from aqueous solutions containing polymers that reversibly bind volatiles (Harrison

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and Hills, 1997b). The presence of binding polymers in the solutions reduces the quantity of free flavor available for release and, hence, perception. The model was based on two assumptions: First, the exchange of flavor molecules between the bound and unbound state was assumed to be extremely fast compared to the transport of flavor across the aqueous−gas interface. Second, the rate-limiting step for flavor release into the headspace was assumed to be mass transfer across the macroscopic aqueous−gas interface. In this section we introduce saliva and gas flows through the respective phases to simulate saliva flow, swallowing, and breathing. The model is based on the combined theories of chemical binding, conservation of flavor mass, and interfacial mass transfer.

Chemical Binding. As the aqueous phase is diluted and flavor is released into the headspace, equilibrium between the concentrations of bound and unbound flavor will be disturbed. The rate of dissociation of the polymer−volatile complex from the bound to the free state is assumed to be a first-order kinetic reaction, which is described by (Harrison and Hills, 1997b)

$$\frac{dc_{bf}(t)}{dt} = \lambda c_{ff}(t) c_b - \mu c_{bf}(t) \tag{1}$$

where c_{bf}, c_b, and c_{ff} correspond to the concentrations of the bound flavor, binder, and free flavor in the aqueous phase, respectively, and where λ and μ are the rate constants.

Conservation of Flavor Mass. For an open system with constant gas flow, q, through the headspace and a saliva flow, Q, through the aqueous phase, conservation of mass is given by

$$\frac{dM}{dt} = v_g \frac{dc_g(t)}{dt} + qc_g(t) = -\left[v_a \frac{dc_a(t)}{dt} + Qc_a(t)\right] \tag{2}$$

where c and v are the concentrations and phase volumes, respectively, and the subscripts a and g denote the aqueous and gas phases, respectively. The flavor in the aqueous phase is comprised of both free and bound flavor

$$c_a(t) = c_{ff}(t) + c_{bf}(t) \tag{3}$$

Inserting eq 3 into eq 2 yields

$$\frac{dM}{dt} = v_g \frac{dc_g(t)}{dt} + qc_g(t) =$$
$$-\left[v_a\left(\frac{dc_{ff}(t)}{dt} + \frac{dc_{bf}(t)}{dt}\right) + Q(c_{ff}(t) + c_{bf}(t))\right] \tag{4}$$

which can be rearranged to give

$$\frac{dc_{ff}(t)}{dt} = -\frac{dc_{bf}(t)}{dt} - \frac{1}{v_a}\left[v_g \frac{dc_g(t)}{dt} + c_g(t) q + Q(c_{ff}(t) + c_{bf}(t))\right] \tag{5}$$

Once the flavor is free in the aqueous phase, it is available for release into the headspace.

Penetration Theory of Interfacial Mass Transfer. The release of flavor into the headspace can be described by the penetration theory of mass transfer, which has been discussed in a previous paper (Harrison
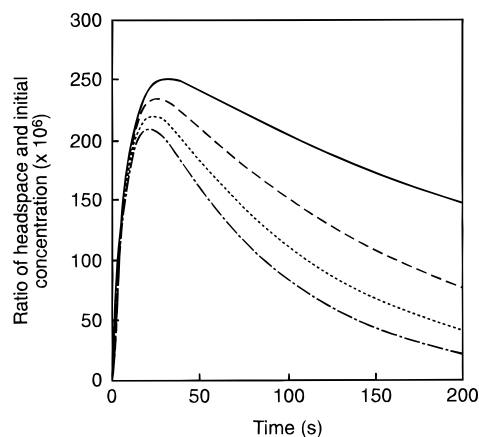
Figure 1. Time-dependent flavor release profiles of diacetyl as a function of the saliva flow rate: $Q = 1$ mL/min, solid line; $Q = 2$ mL/min, dashed line; $Q = 3$ mL/min, dotted line; $Q = 4$ mL/min, dash−dot line.

Table 1. Partition Coefficients for Diacetyl and Heptanone at 25 °C

partition coeffs	diacetyl		heptanone	
	b	c	b	c
K_{gw}[a]	0.32×10^{-3}	0.7×10^{-3}	6.4×10^{-3}	6.2×10^{-3}
K_{go}[a]	0.91×10^{-3}	2.4×10^{-3}	0.25×10^{-3}	0.2×10^{-3}
K_{ow}[a]	0.35	0.29	25.5	31.0

[a] K_{gw}, gas−water partition coefficient; K_{go}, gas−oil partition coefficient; K_{ow}, oil−water partition coefficient. [b] Harrison et al., 1997. [c] Overbosch et al., 1991.

and Hills, 1997b), and is given by

$$\frac{dM}{dt} = h_D A_{ga}\left[c_{ff}(t) - \frac{c_g(t)}{K_{ga}}\right] \tag{6}$$

where M is the total mass of volatile that diffuses across the interface, h_D is the mass transfer coefficient, A_{ge} is the surface area of the interface, and K_{ga} is the gas−liquid partition coefficient. Combining eq 6 and the left-hand side of eq 4, we obtain the following:

$$\frac{dc_g(t)}{dt} = \frac{h_D A_{ga} c_{ff}(t)}{v_g} - \frac{c_g(t)}{v_g}\left[q - \frac{h_D A_{ga}}{K_{ga}}\right] \tag{7}$$

The time-dependent release curves can be obtained by numerically evaluating the three equations describing chemical binding (eq 1), mass conservation (eq 5), and interfacial mass transfer (eq 7) simultaneously. This was achieved using a commercial software package (SimuSolv, Dow Chemical Company, Midland, MI) ran on a VAX 4420. CPU time was approximately 30 s.

THEORETICAL ANALYSIS

Effect of Varying the Saliva and Gas Flows. The rate and extent to which flavor is released from the aqueous phase will primarily depend on the concentration of free flavor in the aqueous and gas phases and therefore will also depend on the rate of volatile removal from the two phases. Figure 1 shows the release of diacetyl from an aqueous solution, with no macromolecules present, as a function of the saliva flow rate. Unless otherwise stated, for this and all proceeding calculations, the values of the various parameters are given in Table 1, with parameters defined in Table 2. Initially the rate of diacetyl release into the headspace

Effect of Saliva Flow on Flavor Release

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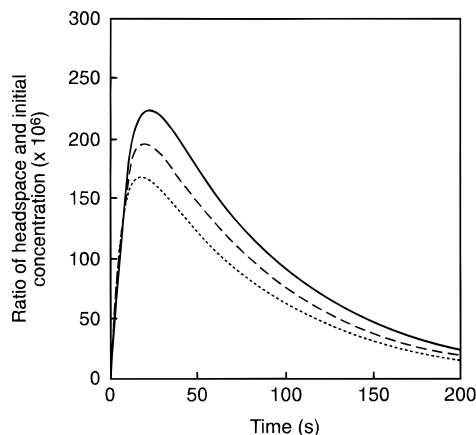
Figure 2. Time-dependent flavor release profiles of diacetyl as a function of the gas flow rate: $Q = 10$ mL/min, solid line; $Q = 50$ mL/min, dashed line; $Q = 100$ mL/min, dotted line.

Table 2. Parameters Used in This Paper

A_{ga}, A_{ge}	area of interface between aq/emulsion and gas phases	4.52×10^{-4} m^2
v_g	vol of gas phase	35 mL
v_a, v_e	vol of aq/emulsion phase	5 mL
q	gas flow rate	30 mL/min
Q	saliva flow rate	3 mL/min
h_D	mass transfer coeff	2.5×10^{-6} m/s
B	binding coeff	1
ϕ	oil vol fraction of emulsion	0.2
d	oil droplet size in the emulsion	1 μm

is independent of the saliva flow rate. At slightly longer times the rate of release decreases and diverges for the different flow rates. After a time, t_{max}, the rate of release from the aqueous phase equals the rate at which flavor is removed from the headspace and a maximum headspace concentration, $c_g(t_{max})$, is obtained.

Both t_{max} and the $c_g(t_{max})$ depend on the saliva flow rates: for fast flow rates t_{max} is attained at slightly shorter times than for the slower saliva flow rates. Furthermore the maximum concentration $c_g(t_{max})$ is also reduced for the faster saliva flow rates. An important feature of Figure 1 is that small increases in saliva flow rate produce very different release profiles. This therefore implies that small differences in flow rates between individuals could produce a variation between flavor release profiles and hence could account for differences in consumer perception of a liquid food product. Conversely, Figure 2 shows that a large variation in the gas flow rate (10−100 mL/min) through the headspace does not influence the flavor release profiles considerably. This therefore, implies that saliva flow and swallowing in the mouth are more important to an individual's perception of a food rather than the rate of breathing. Most liquid foods, however, are not composed entirely of water, as simple and/or complex molecules will usually be present. Furthermore, in the mouth liquid foods will be mixed with saliva, which itself contains a variety of macromolecules. It is therefore highly likely that a proportion of flavor will be complexed and therefore unavailable for release.

Effect of Varying the Rate Constants. As the free flavor is depleted from the aqueous phase, fast exchange between the bound and unbound state will occur in order to maintain equilibrium and in doing so replenishes the free flavor available for release into the headspace. However, our calculations predict that the rate constants λ and μ do not influence the rate of release and hence suggests that the dissociation of the

aroma−polymer complex is not the rate-limiting step, even when the complex dissociation was slow in comparison to partitioning into the headspace. This result is in agreement with previous work (Harrison and Hills, 1997b).

We therefore no longer need to consider the rate constants when predicting which factors control flavor release. Instead, we can assume that the aroma−polymer interaction is always at equilibrium and write (Overbosch et al., 1991)

$$c_{bf} = Bc_{ff} \qquad (8)$$

where c_{bf} and c_{ff} are the concentrations of the bound and free flavors, respectively, and B is the binding coefficient. Differentiating eq 8 and substituting into eq 4 to gives

$$v_g \frac{dc_g(t)}{dt} + qc_g(t) = -(1 + B)\left[v_a \frac{dc_{ff}(t)}{dt} + Qc_{ff}(t)\right] \qquad (9)$$

Once the flavor is free in the aqueous phase, it is available for release into the headspace, which again is described by mass transfer (eq 7). In Appendix A we show, by the method of Laplace transforms, that the solution to the two coupled differential equations (eqs 7 and 9) is

$$c_g(t) = \frac{A_{ga}h_D}{v_g} \frac{c_a(0)}{(1 + B)}\left[\frac{\exp(-s_1 t) - \exp(-s_2 t)}{s_2 - s_1}\right] \qquad (10)$$

where s_1 and s_2 are given by

$$s_1 = \frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4\beta}}{2} \qquad (11)$$

and

$$s_2 = \frac{\alpha}{2} - \frac{\sqrt{\alpha^2 - 4\beta}}{2} \qquad (12)$$

with

$$\alpha = \frac{Q}{v_a} + \frac{q}{v_g} + \frac{A_{ga}h_D}{v_g K_{ga}} + \frac{A_{ga}h_D}{v_a(1 + B)} \qquad (13)$$

and

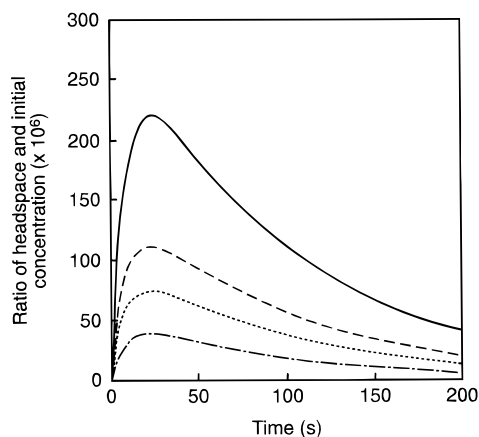$$B = \frac{A_{ga}h_D q}{v_a v_g(1 + B)} + \frac{A_{ga}h_D Q}{K_{ga}v_a v_g} + \frac{Qq}{v_a v_g} \qquad (14)$$

Equation 10 is the desired result.

In the limit of no gas or saliva flow, i.e., $q = 0$ and $Q = 0$, the roots s_1 and s_2 reduce to

$$s_1 = \frac{A_{ga}h_D}{v_g K_{ga}} + \frac{A_{ga}h_D}{v_a(1 + B)} \qquad (15)$$

and

$$s_2 = 0 \qquad (16)$$

Figure 3. Time-dependent flavor release profiles of diacetyl as a function of the binding coefficient: $B = 0$, solid line; $B = 1$, dashed line; $B = 2$, dotted line; $B = 5$, dash−dot line.

and hence eq 10 simplifies to

$$c_g(t) = \frac{A_{ga}h_D}{\nu_g}\frac{c_a(0)}{(1+B)} \times \left[1 - \exp\left\{-\frac{A_{ga}h_D}{\nu_g}\left(\frac{1}{K_{ga}} + \frac{\nu_g}{\nu_a(1+B)}\right)t\right\}\right] \quad (17)$$

This result (eq 17) is identical to that obtained previously (Harrison and Hills, 1997b). We now explore the consequences of the more general formulation (eq 10).

Short Time Effects. Once ingested, flavor would be immediately released from the liquid into the oral cavity as there is no rigid matrix requiring mastication. It is therefore highly unlikely that liquids reside in the mouth for long periods of time. We are therefore concerned with flavor release over very short time scales. At short times the exponential terms in eq 10 can be expanded to first order and predicts a linear time dependence:

$$c_g(t) = \frac{h_D A_{ga}}{\nu_g}\frac{c_a(0)}{1+B}t \quad (18)$$

Again, this result is identical to that obtained previously by Harrison and Hills (1997b) for flavor release from liquids containing aroma-binding macromolecules into a closed headspace. Moreover, eq 18 predicts that the initial rate of flavor release into the headspace is independent of either the gas or saliva flow rates. This result is confirmed by Figures 1 and 2. Furthermore, eq 18 predicts that the main factors controlling the initial rate of release are the original flavor composition and mass transfer coefficient, which itself is primarily determined by the viscosity of the ingested liquid. In all of the previous calculations we have not considered the effects of viscosity on the mass transfer coefficient. Instead it has been assumed that the presence of dilute mixtures of macromolecules will not alter the viscosity.

Effect of Varying the Binding Coefficient. Figure 3 shows time-dependent release profiles of diacetyl as a function the of the binding coefficient, B. As the binding coefficient increases, the initial rate of flavor release decreases in accordance with eq 16. At slightly longer times the rate of release decreases, and after a time t_{max} the rate of release from the liquid mixture equals the rate at which flavor is removed by the gas
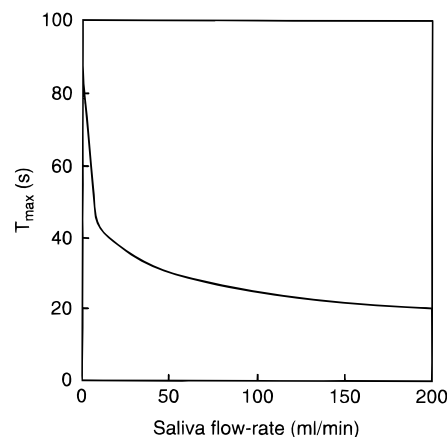
Figure 4. Time required to reach maximum headspace concentration, t_{max}, as a function of the saliva flow rate.

flow and, hence, coincides with a maximum concentration, $c_g(t_{max})$, of flavor in the headspace. We now look more closely at the effect of the saliva flow rate and binding coefficient on t_{max} and $c_g(t_{max})$.

Time To Reach Maximum Flavor Concentration, t_{max}. In Appendix B we derive an expression for the time to reach maximum flavor intensity in the headspace:

$$t_{max} = \frac{1}{(s_1 - s_2)}\ln\left(\frac{s_2}{s_1}\right) \quad (19)$$

Here s_1 and s_2 are given by eqs 11 and 12, respectively. It is interesting to note that eq 19 predicts that the time to reach maximum flavor concentration is independent of the initial concentration, $c_a(0)$ but depends critically on the gas and saliva flow rates, q and Q, the mass transfer coefficient, h_D, and the gas−liquid partition coefficient, K_{ga}. Figure 4 shows t_{max} of diacetyl decreasing exponentially with increasing saliva flow rate. In this calculation we have taken B to be equal to 1; however, our calculations showed that the relationship between Q and t_{max} illustrated in Figure 4 is almost identical for all values of the binding coefficient. This result was first observed in Figure 3.

Maximum Flavor Concentration, $c_g(t_{max})$. The maximum flavor concentration in the headspace at t_{max} can be determined by substituting the equation for t_{max} (eq 19) into the release equation (eq 7) to give

$$c_g(t_{max}) = \frac{A_{ge}h_D c_a(0)}{\nu_g(1+B)}\left[\frac{\exp(-s_1 t_{max}) - \exp(-s_2 t_{max})}{s_2 - s_1}\right] \quad (20)$$

where s_1 and s_2 are given by eqs 11 and 12, respectively. Equation 20 shows that $c_g(t_{max})$ is proportional to the initial flavor concentration in the aqueous phase, $c_a(0)$. Not surprisingly the other parameters controlling the maximum flavor concentration are the partition coefficient, the mass transfer coefficient, and the flow rates. Figure 5 shows the maximum headspace concentration, $c_g(t_{max})$, of diacetyl decreasing exponentially with an increasing saliva flow rate for three binding coefficients. Furthermore, Figure 4 shows that a stronger aroma−polymer interaction has a greater influence on the maximum headspace concentration than the saliva flow rate.

Effect of Saliva Flow on Flavor Release

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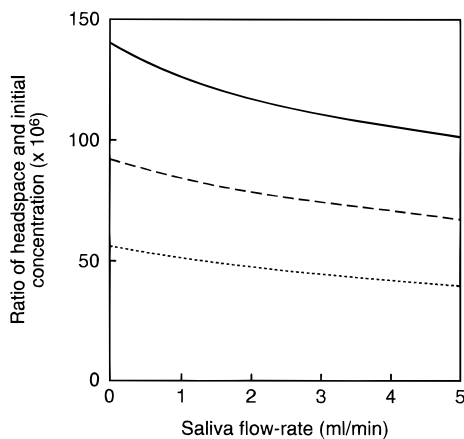
Figure 5. Maximum headspace concentration, $c_g(t_{max})$, as a function of the saliva flow rate for varying binding coefficients, B: $B = 1$, solid line; $B = 2$, dashed line; $B = 4$, dotted line.

The effect therefore of introducing interactions between volatiles and macromolecules is to reduce both the rate and the extent of flavor release in the mouth. The majority of liquid foods contain lipids in addition to macromolecules. In fact lipids often have a greater effect on the flavor release profiles from foods than both polysaccharides and proteins. In the next section we focus on the effects of saliva dilution on liquid emulsions in the mouth.

THEORY OF FLAVOR RELEASE FROM EMULSIONS

Theory. Previously, a mathematical model was developed to examine the effect of a gas flow rate on flavor release from liquid emulsions (Harrison and Hills, 1997a). These authors found that in general the initial rates of release were faster for emulsions of lower oil content and the maximum flavor concentration in be the headspace was found to be linearly proportional to the initial flavor concentration. In this section we introduce a saliva flow through the emulsion phase to examine the effects of diluting the oil phase. In developing this model, we have assumed that the rate-limiting step for release is the transfer of volatiles across the emulsion–gas interface. We further assume that the partitioning off flavor molecules between the oil and aqueous phases was extremely rapid compared to the transport of flavor across the emulsion–gas interface (Harrison et al., 1997). The model was therefore again based on the combined theories of interfacial mass transfer and conservation of flavor mass.

Penetration Theory of Interfacial Mass Transfer. Once again flavor transfer across the emulsion–gas interface can be described by the penetration theory of mass transfer (Harrison et al., 1997)

$$\frac{dM}{dt} = h_D A_{ga}\left[c_e(t) - \frac{c_g(t)}{K_{ge}}\right] \qquad (21)$$

where M is the total mass of volatile that diffuses across the interface, h_D is the mass transfer coefficient, A_{ge} is the surface area of the interface, and c_e and c_g denote the concentration of flavor in the emulsion and gas phases, respectively. The parameter K_{ge} in eq 21 is the gas–emulsion partition coefficient and is given by

(Overbosch et al., 1991)

$$K_{ge} = \frac{K_{gc}}{1 + (K_{dc} - 1)\phi_d} \qquad (22)$$

where K_{gc} and K_{dc} are the equilibrium partition coefficients between the gas and continuous phases and between the dispersed and continuous phases, respectively.

The mass transfer coefficient, h_D, is an important physical parameter controlling the rate of flavor release into the headspace. One factor greatly influencing h_D is the emulsion shear viscosity, η, since this determines the rate of diffusion of flavor molecules across the interface. The shear viscosity will increase with increasing oil fraction, ϕ, and will also depend on the droplet size distribution within the emulsion (Sherman, 1968; Thomas, 1965). For many simple emulsions the relationship between h_D, ϕ, and the mean droplet size, d (in μm) can be written as (Harrison et al., 1997)

$$h_D(\phi,d) = h_D(0)\,\exp\left[-\frac{b}{2}(\ln 10)\left(\frac{\phi}{d}\right)\right] \qquad (23)$$

where $h_D(0)$ is the mass transfer coefficient of a particular flavor compound from water and b is a constant equal to 2.72.

A saliva flow through the liquid phase will dilute the emulsion thus reducing the oil fraction. The rate of oil loss from the emulsion phase can be described mathematically by

$$\frac{dv_o(t)}{dt} = -Q \qquad (24)$$

where $v_o(t)$ is the time-dependent volume of oil present in the liquid phase. Equation 24 can be written in terms of the oil fraction by dividing both sides of the equation by v_e

$$\frac{d\phi(t)}{dt} = -\frac{Q}{v_e} \qquad (25)$$

Integrating eq 25 with respect to time yields a time-dependent expression for the oil fraction

$$\phi(t) = \phi(0)\exp\left(-\frac{Qt}{v_e}\right) \qquad (26)$$

where $\phi(0)$ is the initial oil volume fraction. As the emulsion is diluted by the saliva flow, the viscosity of the liquid phase will decrease, which is reflected in an increased mass transfer coefficient. The eq 22 will therefore become time-dependent, and during the course of the dilution flavor will be more readily released from the liquid phase into the headspace. Furthermore, as the emulsion is diluted, the partitioning of volatiles between the oil and aqueous phases are disturbed and hence the partition coefficient between the emulsion and headspace (eq 22) is also time-dependent.

Conservation of Flavor Mass. For an open system, such as that described above, conservation of flavor mass yields

$$\frac{dM}{dt} = v_g\frac{dc_g(t)}{dt} + qc_g(t) = -\left[v_e\frac{dc_e(t)}{dt} + Qc_e(t)\right] \qquad (27)$$
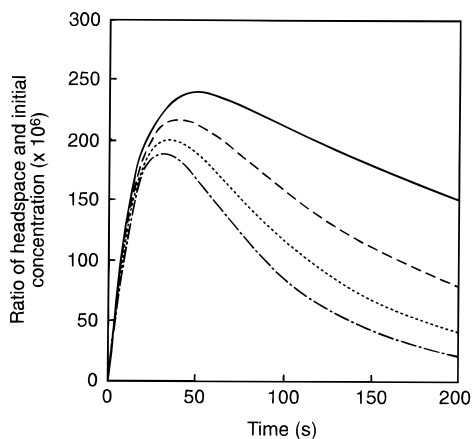
Figure 6. Time-dependent release profiles of diacetyl released from a 20/80 oil-in-water emulsion as a function of the saliva flow rate: $Q = 1$ mL/min, solid line; $Q = 2$ mL/min, dashed line; $Q = 3$ mL/min, dotted line; $Q = 4$ mL/min, dashed−dotted line.

Figure 7. Time-dependent mass transfer coefficient as a function of the saliva flow rate: $Q = 1$ mL/min, solid line; $Q = 2$ mL/min, dashed line; $Q = 3$ mL/min, dotted line; $Q = 4$ mL/min, dashed−dotted line.

Figure 8. Time-dependent release profiles of heptan-2-one released from emulsions of varying oil fraction: $\phi = 0.01$, solid line; $\phi = 0.05$, dashed line; $\phi = 0.1$, dotted line; $\phi = 0.3$, dashed−dotted line.

where Q and q denote the saliva and gas flow rates through the respective phases. Rearranging eq 27 for $c_g(t)$ gives

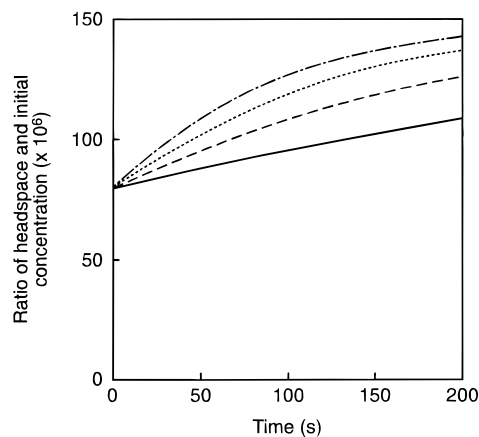$$\frac{dc_g(t)}{dt} = -\frac{1}{v_g}\left[v_e\frac{dc_e(t)}{dt} + Qc_e(t) + qc_g(t)\right] \quad (28)$$

A second nonlinear differential equation is obtained from combining eq 21 and the right-hand side of eq 27:

$$\frac{dc_e(t)}{dt} = c_g(t)\left[\frac{A_{ge}h_D}{v_eK_{ge}}\right] - c_e(t)\left[\frac{Q}{v_e} + \frac{A_{ge}h_D}{v_e}\right] \quad (29)$$
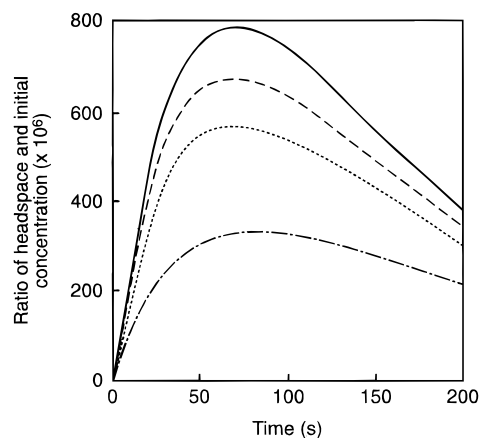
The time-dependent release curves of the concentration of flavor in the headspace can be obtained by numerically evaluating these coupled differential equations (eqs 27 and 29) simultaneously. Again this was achieved using a commercial software package (Simu-Solv, Dow Chemical Co., Midland, MI) ran on a VAX 4420. CPU time was approximately 30 s. Using this software package we can look at the effect of varying the saliva flow rate and emulsion structure on flavor release from liquid emulsions.

THEORETICAL ANALYSIS

Effect of Varying the Saliva Flow Rate. Figure 6 shows the time-dependent release profiles of diacetyl from a 20/80 oil-in-water emulsion as a function of the saliva flow rate, Q. At shorter times the rate of release is independent of the saliva flow rate, a result which is not derivable here but is expected in light of previous work on liquid emulsions (Harrison et al., 1997; Harrison and Hills, 1997a). At slightly longer times the rates of release decrease depending on the saliva flow rate and a maximum concentration in the headspace, $c_g(t_{max})$, is attained after a time t_{max}. Both of the parameters t_{max} and $c_g(t_{max})$ depend on the saliva flow rate, Q. For an increasing saliva flow rate both $c_g(t_{max})$ and t_{max} decrease as flavor is more quickly removed from the liquid phase and thus is unavailable for release into the headspace. In light of this result a greater difference between $c_g(t_{max})$ for the variation of saliva flow rates might be expected. However, a more rapid dilution of the emulsion decreases the viscosity of the

aqueous phase and thus increases the mass transfer coefficient (Figure 7) and therefore the rate of release.

At times longer than t_{max} the concentration of flavor in the headspace decreases exponentially with time, the rate of which is determined by the value of Q. Faster saliva flow rates result in a more rapid clearing of the oil from the mouth. This result may partially explain differences in an individual's perception of an emulsion-based product in the latter stages of consumption.

Effect of Varying the Oil Properties of the Emulsion. The composition of an emulsion determines both the structural and physicochemical properties of the food product. Changing either the quantity or type of oil can have dramatic effects on the rates of flavor release: first, the distribution of volatiles in an emulsion will depend on both the oil fraction and the partitioning properties between the oil and aqueous phases and, second, alter the emulsion shear viscosity and therefore the interfacial mass transfer properties. In this section we investigate the effect of changing the oil fraction, mass transfer coefficient, and oil−water partition coefficient on flavor release from liquid emulsions in the presence of both saliva and gas flows.

Figure 8 shows that the maximum flavor concentration of heptan-2-one in the headspace, $c_g(t_{max})$, decreases with increasing oil fraction. However, more interestingly Figure 8 shows that the time to attain maximum
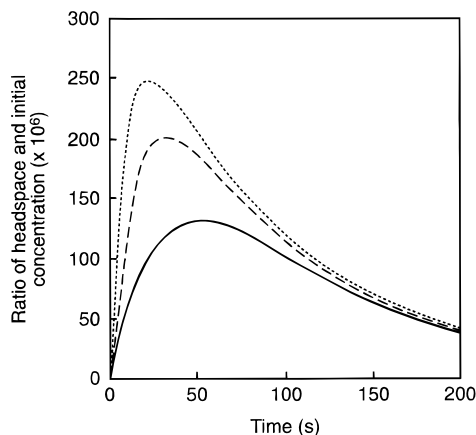
Figure 9. Time-dependent release profiles of diacetyl released from emulsions possessing varying mass transfer coefficients: $h_D = 1 \times 10^{-6}$ m/s, solid line; $h_D = 2.5 \times 10^{-6}$ m/s, dashed line; $h_D = 5 \times 10^{-6}$ m/s, dotted line.
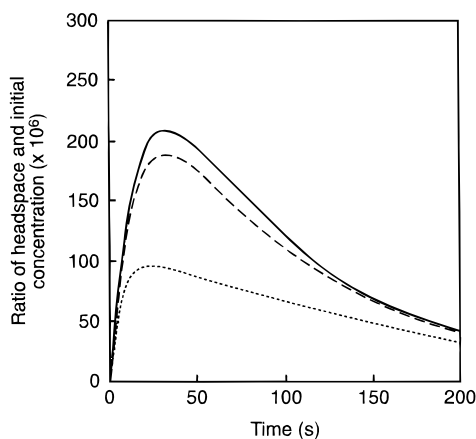
Figure 10. Time-dependent release profiles of a volatile from a 20/80 oil-in-water emulsion for varying values of the oil–water partition coefficient: $K_{ow} = 0.1$, solid line; $K_{ow} = 1$, dashed line; $K_{ow} = 10$, dotted line.

flavor concentration in the headspace, t_{max}, is unaffected by reducing the oil fraction. Unfortunately, due to the complexity of the mathematics it is not possible to derive an analytical expression for either t_{max} or $c_g(t_{max})$. Instead eqs 27 and 29 have to be evaluated numerically for each time-dependent release curve. Figure 8 also shows that the initial release rate of heptan-2-one release into the headspace decreases with increasing the oil fraction. This result agrees with the previous work of Harrison and Hills (1997a), which predicts that at short times the rate of flavor release is linearly proportional to the mass transfer coefficient, which is dependent on both the oil fraction and droplet size (eq 25).

Replacing one lipid in an emulsion with another will change both the viscosity and the oil–water partitioning properties. The dependence of the mass transfer coefficient on flavor release is illustrated in Figure 9, which shows that $h_D(0)$ alone has a large influence on flavor release profiles in systems which are continuously being diluted. In addition to controlling the initial rate of release, the mass transfer coefficient greatly influences both t_{max} and $c_g(t_{max})$, as does the oil–water partition coefficient, K_{ow}. Figure 10 shows that for greater values of K_{ow} the quantity of flavor released into the headspace decreases. This result is observed because the volatiles increasingly prefer to partition into the oil phase and are therefore less likely to be released into the headspace via the aqueous phase.

As the consumer has become increasingly aware of connection between diet and health, food companies have developed new products with either reduced or no fat by using a wide range of fat-replacers. However, the public's acceptance of these products has been somewhat poor. The model presented in this paper could be used by a food technologist to examine the effects of saliva dilution on liquid foods. This can be achieved by instrumentally monitoring volatile concentrations in the out-flowing gas with time. By comparing of the release profiles of low-fat products with the more traditional high-fat foods, flavorists would then be able to reformulate the flavor composition of a product.

CONCLUSIONS

In this paper we have presented a mathematical model of the flavor release kinetics from liquid foods in the mouth that explicitly treat the effects of breathing and saliva dilution. Two types of liquid foods have been considered: first, aqueous solutions containing aroma-binding macromolecules and, second, liquid oil-in-water emulsions. Both models are based on the assumption that the rate-limiting step is the resistance to mass transfer across the liquid–gas interface, which is described by the penetration theory. Furthermore, as in previous models describing flavor release from liquid emulsions, we assumed that partitioning of flavor molecules between the oil and aqueous phases is extremely rapid compared to the transport of flavor across the emulsion–gas interface.

In general initial rates of release were found to be linearly dependent on time and proportional to the initial flavor concentration and mass transfer coefficient. More surprisingly our results show that the initial rates of release are independent of both the gas and saliva flow rates. This result, therefore, implies that it is the structure and composition of the food that determines the initial rates of flavor release. In the case of liquid emulsions factors such as the oil fraction, type of oil and droplet size will influence the initial rate of release. At slightly longer times the rate of release decreases and is sensitive to the saliva flow rate (Figures 1 and 6), reaching a maximum concentration, $c_g(t_{max})$, after a time t_{max}. This implies that the variation of saliva flow rates found between individuals (Noble, 1995) may partially account for differences in perception of a food product. The theory also shows that both t_{max} and $c_g(t_{max})$ are sensitive to other factors such as the mass transfer, binding, and partition coefficients.

For the case of liquids containing aroma-binding macromolecules it was originally assumed that the rate of exchange of volatiles between the bound and unbound states can be described by first-order chemical kinetics. However, in agreement with previous work (Harrison and Hills, 1997b), the results show that the rate constants describing the kinetic reaction do not influence the release profiles and, hence, are not rate limiting even in a dynamic system such as the mouth. By assuming that the aroma–polymer interaction is always at equilibrium, an analytical theory for the time-dependent flavor concentration in the gas phase was developed. From this theory expressions for both t_{max} and $c_g(t_{max})$ were derived. Somewhat surprisingly, this theory predicts that t_{max} is independent of the initial flavor concentration and only very slightly dependent on the binding coefficient. Conversely, $c_g(t_{max})$ is proportional to the initial flavor concentration and greatly

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dependent on the binding coefficient as the presence of binding polymers reduces the quantity of free flavor available for release and hence perception.

In this paper we have focused on the effects of saliva dilution on flavor release from liquid foods. However, the majority of foods are solid and volatiles first have to be released from the food matrix into the saliva phase. This may occur through a number of mechanisms, such as dissolution (Hills and Harrison, 1995), melting (Harrison and Hills, 1996), or hydration (Ingham, 1997) of the food matrix. Moreover, the majority of foods first need to be broken down, by the process of mastication, into smaller particles before being mixed and diluted with saliva. The next, and more complicated, step is to therefore incorporate mastication of the food matrix in these models and this will be the subject of future work.

APPENDIX A

First, we take Laplace transforms of eq 7 in the main text to yield

$$v_g[sc_g(s)] = \frac{h_D A_{ga} c_{ff}(s)}{v_g} - \frac{c_g(s)}{v_g}\left[q - \frac{h_D A_{ga}}{K_{ga}}\right] \quad (A1)$$

Here it has been assumed that the initial flavor in the headspace, $c_g(0)$, is zero. Rearranging eq A1 gives

$$c_g(s)\left[v_g s + q + \frac{A_{ga} h_D}{K_{ga}}\right] + c_{ff}(s)[-A_{ga} h_D] = 0 \quad (A2)$$

which can be written in the form

$$ec_g(s) + fc_{ff}(s) = 0 \quad (A3)$$

where

$$e = v_g s + q + \frac{A_{ga} h_D}{K_{ga}} \quad (A4)$$

and

$$f = -A_{ga} h_D \quad (A5)$$

Now take Laplace transforms of eq 9 in the main text to give

$$v_g sc_g(s) + qc_g(s) = -(1 + B)[v_a(sc_{ff}(s) - c_{ff}(0)) + Qc_{ff}(s) \quad (A6)$$

Again it has been assured that the initial flavor in the headspace, $c_g(0)$, is zero. Rearranging eq A6 in the form of eq A3 gives

$$gc_g(s) + hc_{ff}(s) = v_a c_a(0) \quad (A7)$$

with

$$g = v_g s + q \quad (A8)$$

and

$$h = (1 + B)(v_a s + c) \quad (A9)$$

and where $c_a(0)$ is the initial flavor concentration in the aqueous phase.

The first step to obtaining a solution for the time dependence of $c_g(t)$ is to write eqs A3 and A7 as

simultaneous equations in matrix form

$$A\begin{pmatrix} c_g(s) \\ c_{ff}(s) \end{pmatrix} = \begin{pmatrix} 0 \\ c_a(0)v_a \end{pmatrix} \quad (A10)$$

where A is given by

$$A = \begin{bmatrix} e & f \\ g & h \end{bmatrix} \quad (A11)$$

Multiplying both sides of eq A10 by A^{-1}, the inverse matrix of (A11) gives

$$\begin{pmatrix} c_g(s) \\ c_{ff}(s) \end{pmatrix} = A^{-1}\begin{pmatrix} 0 \\ c_a(0)v_a \end{pmatrix} \quad (A12)$$

The time dependence of the flavor concentration in the gas phase is then given by

$$c_g(s) = -\frac{f}{\det A}v_a c_a(0) \quad (A13)$$

where f is given by eq A5 and det A by

$$\det A = -v_a v_g(1 + B)[s^2 + s\alpha + \beta] \quad (A14)$$

where

$$\alpha = \frac{Q}{v_a} + \frac{q}{v_g} + \frac{A_{ga} h_D}{v_g K_{ga}} + \frac{A_{ga} h_D}{v_a(1 + B)} \quad (A15)$$

and

$$\beta = \frac{A_{ga} h_D q}{v_a v_g(1 + B)} + \frac{A_{ga} h_D Q}{K_{ga} v_a v_g} + \frac{Qq}{v_a v_g} \quad (A16)$$

Equation A14 can be written in the form

$$\det A = -v_a v_g(1 + B)(s + s_1)(s + s_2) \quad (A17)$$

where the roots are given by the quadratic formula

$$s_1 = \frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4\beta}}{2} \quad (A18)$$

and

$$s_2 = \frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4\beta}}{2} \quad (A19)$$

The expression for the determinant eq A17 can now be substituted into eq A13 to give

$$c_g(s) = \frac{A_{ga} h_D}{v_g} \frac{c_a(0)}{(1 + B)}\left[\frac{1}{(s + s_1)(s + s_2)}\right] \quad (A20)$$

The inverse Laplace transforms of eq A20 is eq 10 in the main text.

APPENDIX B

At the point of maximum flavor concentration in the headspace, $c_g(t_{max})$, the differential of eq 10, with respect

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to time, will be equal to zero, *i.e.*

$$\frac{dc_g(t)}{dt} = -\frac{A_{ge}h_D c_a(0)}{v_g(1+B)}$$
$$\left[\frac{s_1 \exp(-s_1 t_{max}) - s_2 \exp(-s_2 t_{max})}{s_1 - s_2}\right] = 0 \quad (B1)$$

For eq B1 to be true the term within the brackets must equal zero, *i.e.*

$$\frac{s_1 \exp(-s_1 t_{max}) - s_2 \exp(-s_2 t_{max})}{s_1 - s_2} = 0 \quad (B2)$$

Now let $s_1 = s_2 + \delta$ and substitute into (B2) to produce

$$\left[\frac{(s_2 + \delta) \exp(-(s_2 + \delta) t_{max}) - s_2 \exp(-s_1 t_{max})}{\delta}\right] = 0 \quad (B3)$$

which can be expanded and rearranged to give

$$\exp(-s_2 t_{max})\left[\frac{s_2}{\delta}\exp(-\delta t_{max}) + \exp(-\delta t_{max}) - \frac{s_2}{\delta}\right] = 0 \quad (B4)$$

Equation B4 is true only if the term in brackets is equal to zero, *i.e.*

$$\frac{s_2}{\delta} \exp(-\delta t_{max}) + \exp(-\delta t_{max}) - \frac{s_2}{\delta} = 0 \quad (B5)$$

and rearrangement of eq B5 gives

$$(s_2 - \delta) \exp(-\delta t_{max}) = s_2 \quad (B6)$$

Substituting $\delta = s_2 - s_1$ back into eq B6 and rearranging for t_{max} produces eq 19 in the main text, where s_1 and s_2 are given by eqs 11 and 12 in the main text.

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