# Mathematical Model of Flavor Release from Liquids Containing Aroma-Binding Macromolecules

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A mathematical model has been developed to describe flavor release from aqueous solutions containing flavor-binding polymers. First-order chemical kinetics is used to describe the reversible binding of the aroma and polymer, and the penetration theory of interfacial mass transfer is used to model flavor release across the gas−liquid interface. The model is used to predict the equilibrium partitioning properties and the rates of release of two volatiles, one hydrophilic (diacetyl) and the other hydrophobic (heptan-2-one), as a function of the binding constants and first-order rate constants. In general, the rates of release are shown to be more sensitive to changes in the binding constant than the rate constants. Increasing the flavor−binder interaction leads to decreased release rates and a lower final headspace aroma concentration. Nevertheless, the results suggest that in most situations the rate-limiting step for flavor release is not the chemical binding step but the transport of aroma across the liquid−gas interface.

## INTRODUCTION

The flavor perception of a particular food product is a major factor determining consumer acceptance. The quantity of flavor released into the oral cavity depends on the retention of flavor compounds in the food matrix and, therefore, on the nature of the ingredient−flavor interactions. Knowledge of the binding behavior of flavor compounds to different food components and their rates of release from the food matrix is therefore of great practical importance in the formulation of new food products.

Interest in flavor binding has also been stimulated by attempts to use biopolymers as fat substitutes, but, so far, this has been of only limited success in terms of consumer acceptance (Plug and Haring, 1993). One possible reason may be that a decrease in fat content results in an increased rate of volatization (Harrison *et al.*, 1997; Harrison and Hills, 1997), thus reducing the perceived flavor quality. Knowledge of the effects of macromolecule flavor binding on release rates could therefore assist in designing low-fat substitutes that give the same flavor release profiles as the original high-fat food.

Experimental studies of flavor binding have been limited to simple aqueous mixtures containing polysaccharides and proteins. Selective binding of a particular volatile to a macromolecule present in a food lessens the effective free concentration available for release and hence can significantly alter the overall flavor available for perception (Overbosch *et al.*, 1991). Various types of flavor−macromolecule binding interaction have been identified, including encapsulation, entrapment, and inclusion complexes (Solms, 1986; Godshall and Solms, 1992) and bond formation (Buttery *et al.*, 1971; Le Thanh *et al.*, 1992). The relative importance of these mechanisms obviously depends on the nature of the flavor and biopolymer, of which polysaccharides and proteins are the major categories.

Polysaccharides can bind to volatiles in a number of ways. Some carbohydrates can bind to volatiles via hydrogen bonding between appropriate functional groups (Maier, 1975). Others, such as starch, consist of three-dimensional structures with hydrophobic regions capable of forming inclusion complexes with various hydrophobic volatiles (Solms, 1986; Godshall and Solms, 1992). Cyclodextrins are capable of entrapping volatiles (Maier, 1975) and have been used to selectively bind certain undesirable off-flavors (Szente and Szejtli, 1988). In addition, cyclodextrins are especially effective in retaining flavor during drying storage and releasing the flavor upon hydration, e.g. in the mouth (Reineccius and Bangs, 1985).

Proteins have also been shown to decrease the headspace concentration of volatiles in both aqueous and dry systems (Solms *et al.*, 1973). Nawar (1973) showed that gelatin decreased the apparent volatility of methyl ketones. Gremli (1974) showed that an aqueous dispersion of soy protein reduced the volatility of aldehydes and, moreover, that the percent decrease in volatility increased with the molecular size of the aldehydes. This result indicated that the magnitude of the interaction was a function of chain length. Franzen and Kinsella (1974) attempted to relate binding between various proteins and aldehydes or ketones to differences in intrinsic binding affinities, protein structure, and available surface area.

Very few mathematical models have been developed to describe time-dependent flavor release from liquid systems, and none have explicitly treated flavor-binding interactions. Darling *et al.* (1986) successfully modeled isopentyl acetate release from galactomannan and sucrose solutions into the headspace. They based their model on the penetration theory of interfacial mass transfer across the liquid−gas interface. They concluded that interfacial surface regeneration is a significant physical factor controlling the release of flavor into the headspace. Harrison *et al.* (1997) developed a mathematical model to describe flavor release from emulsions based on the assumption that the rate-limiting step is the transfer of flavor across the emulsion−gas interface. They assumed that partitioning of

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**1884**  *J. Agric. Food Chem.,* Vol. 45, No. 5, 1997

Harrison and Hills

flavor molecules between the oil and aqueous phases is extremely rapid compared to the transport of flavor across the emulsion–gas interface. The model suggests that the major physical factors affecting the rate of flavor release include the mass transfer coefficient, $h_D$, the initial emulsion concentration, $c_e(0)$, and the gas–emulsion partition coefficient, $K_{ge}$. None of this work, however, considered the binding of volatiles to the macromolecules present in the solutions.

In this paper we present a mathematical model of flavor release into the headspace from liquid mixtures containing binding polymers. The model incorporates the penetration theory of interfacial mass transfer to describe flavor transport across the liquid–gas interface and first-order chemical kinetics to describe the interaction between flavor and ingredient. We use this model to identify which of the physicochemical factors control the rate of flavor release from such liquid mixtures.

BINDING

In a solution containing flavor and binding polymers a proportion of flavor will bind to the polymer and only the free flavor will be readily available in the mouth for perception. The total flavor in the solution is given by

$$c_{tf} = c_{bf} + c_{ff} \tag{1}$$

where $c_{tf}$, $c_{bf}$, and $c_{ff}$ are the total, bound, and free flavor concentrations, respectively. For simplicity we assume that flavor release can be described by the reversible first-order reaction

$$\underset{c_{bf}}{BF} \underset{\lambda}{\overset{\mu}{\rightleftharpoons}} \underset{c_b}{B} + \underset{c_{ff}}{F}$$
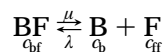
where $c_{bf}$, $c_b$, and $c_{ff}$ correspond to the concentrations of the bound flavor, binder, and free flavor in the aqueous phase, respectively. Assuming first-order kinetics we can write

$$\frac{dc_{ff}(t)}{dt} = \mu c_{bf}(t) - \lambda c_{ff}(t) c_b(t) \tag{2}$$

The equilibrium situation is obtained when $dc_{ff}(t)/dt$ is zero, when

$$\frac{c_{bf}^e}{c_{ff}^e c_b^e} = \frac{\lambda}{\mu} = K_b \tag{3}$$

where $c_{bf}^e$ and $c_{ff}^e$ are the equilibrium concentrations of the bound and free flavors, respectively, $c_b^e$ is the equilibrium concentration of binder present in the solution, and $K_b$ is the equilibrium binding constant. Since it is reasonable to assume that the concentration of free binder will greatly exceed the concentration of the binder–flavor complex, $c_{bf}^e$, then $c_b^e$ can in effect be regarded as the total concentration of binder in the mixture, $c_b$, and therefore becomes time-independent. If eq 1 is then substituted into eq 3 and rearranged for $c_{ff}^e$, it is easy to obtain

$$c_{ff}^e = \frac{c_{tf}^e}{1 + K_b c_b} \tag{4}$$



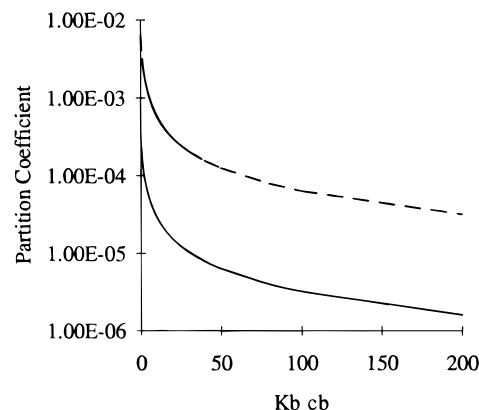**Figure 1.** Partition coefficients of diacetyl (solid line) and heptan-2-one (dashed line) as a function of the product $K_b c_b$. $K_{ga}$ values are $3.2 \times 10^{-4}$ and $6.4 \times 10^{-3}$ for diacetyl and heptan-2-one, respectively (Harrison *et al.*, 1997).

This result (eq 4) demonstrates that the addition of binders reduces the free equilibrium flavor concentration by a factor of $(1 + K_b c_b^e)$. This is reflected in the gas–liquid partition coefficient, which is also reduced by the same factor to produce an effective partition coefficient, $K_{ga}^{eff}$:

$$K_{ga}^{eff} = \frac{c_g^e}{c_{ff}^e} = \frac{K_{ga}}{1 + K_b c_b} \tag{5}$$

Figure 1 shows that the effective partition coefficient (eq 5) decreases with an increasing product $K_b c_b$ for both a hydrophilic (diacetyl) and a hydrophobic (heptan-2-one) flavor compound. In this calculation it has been assumed that the partition coefficients in the absence of binding are $3.2 \times 10^{-4}$ and $6.4 \times 10^{-3}$ for diacetyl and heptan-2-one, respectively (Harrison *et al.*, 1997).

THEORY OF FLAVOR RELEASE FROM SOLUTIONS

The rate of flavor release can be derived from the three basic equations describing chemical binding, mass conservation, and interfacial mass transfer.

**Chemical Binding.** As 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 given by eq 2. However, to describe the rate of change of free flavor concentration, we must also take into account the release of free flavor from the aqueous phase into the headspace. This is achieved by subtracting an extra term, $(v_g/v_a)dc_g(t)/dt$, from the right-hand side of eq 2:

$$\frac{dc_{ff}(t)}{dt} = \mu c_{bf}(t) - \lambda c_{ff}(t) c_b - \frac{v_g}{v_a}\frac{dc_g(t)}{dt} \tag{6}$$

**Conservation of Mass of Aroma.** For a closed system conservation of mass yields

$$\frac{dM}{dt} = v_g\frac{dc_g(t)}{dt} = -v_a\frac{dc_{tf}(t)}{dt} \tag{7}$$

where $c$ and $v$ are the concentrations and phase volumes, respectively, and the subscripts g and a denote the gas and aqueous phases, respectively. The flavor in the aqueous phase is comprised of both free and bound flavor (eq 1); hence, eq 7 can be written
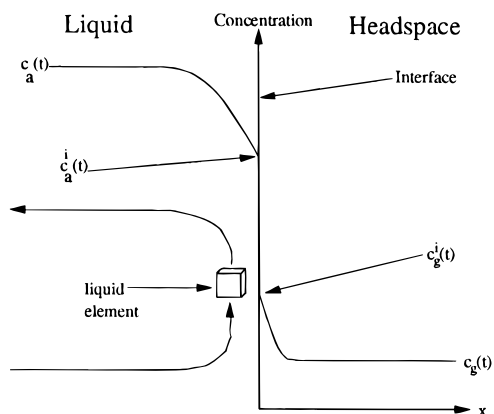
Flavor Release from Liquids Containing Aroma-Binding Polymers

*J. Agric. Food Chem.,* Vol. 45, No. 5, 1997 **1885**



**Figure 2.** Schematic diagram of flavor release across an interface (solid vertical line). Partitioning of the volatiles and efficient mixing of the phases produce the concentrations illustrated. In the penetration model of interfacial mass transfer a volume element of liquid from the bulk comes into contact with the interface layers and is exposed to the second phase for a definite interval of time. During this time, equilibrium is attained by the surface layers through a process of un-steady-state molecular diffusion of flavor into the gaseous phase, before the volume element is remixed with the bulk liquid.

$$\frac{\mathrm{d}M}{\mathrm{d}t} = v_g \frac{\mathrm{d}c_g(t)}{\mathrm{d}t} = -v_a\left[\frac{\mathrm{d}c_{ff}(t)}{\mathrm{d}t} + \frac{\mathrm{d}c_{bf}(t)}{\mathrm{d}t}\right] \qquad (8)$$

Once the flavor is free in the aqueous phase, it is available for release into the headspace. The release of flavor into the headspace can be described by the penetration theory of mass transfer.

**Penetration Theory of Interfacial Mass Transfer.** In penetration theory it is assumed that because the liquid phase is agitated, an element of liquid, whose initial composition corresponds with that of the bulk, is brought to the interface where it is exposed to the second phase for a definite interval of time, $t_e$ (Figure 2). Thus, liquid remote from the interface is suddenly exposed to the second phase. During this time interfacial transport between the surface layers proceeds through a process of un-steady-state molecular diffusion of flavor into the second phase. The driving force for flavor release across the interface is the nonequilibrium concentration difference for volatiles between the emulsion and the vapor phase in the mouth. Then, after a time $t_e$ the volume element is remixed with the bulk. The rate of mass transfer across the interface is given by (Coulson and Richardson, 1993)

$$\frac{\mathrm{d}M}{\mathrm{d}t} = 2\sqrt{\frac{D_a}{\pi t_e}} A_{ga}[c_a^i(t) - c_a(t)] \qquad (9)$$

where $M$ is the total mass of volatile that diffuses across the interface, $D_a$ is the average diffusion coefficient of the free flavor molecules in the emulsion, $A_{ge}$ is the surface area of the interface, $t_e$ is the time that each surface element is exposed to the interface, and $c_e^i(t)$ and $c_e(t)$ are the concentrations of volatile at the interface and within the bulk, respectively. Because $t_e$ cannot be measured independently $2(D_a/\pi t_e)^{1/2}$ is usually replaced by a single parameter (the mass transfer coefficient), $h_D$. If we assume that the mean contact time of a fluid element at the interface is proportional to the reciprocal of the stirring rate, $J$ (Darling *et al.*, 1986), then $h_D$ is predicted to vary as the square root of $J$.

In general, the concentrations at the surfaces will not be known, but if we assume that the gaseous phase is perfectly stirred, the concentration of flavor in the gas phase at the interface will be equal to that in the bulk, *i.e.* $c_g^i(t) = c_g(t)$. Substituting this approximation into eq 9 yields

$$\frac{\mathrm{d}M}{\mathrm{d}t} = h_D A_{ga}\left[c_{ff}(t) - \frac{c_g(t)}{K_{ga}}\right] \qquad (10)$$

Now, equating the expressions for mass conservation (eq 7) and interfacial mass transfer (eq 10) gives an expression for the rate of change of flavor concentration in the gaseous phase

$$\frac{\mathrm{d}c_g(t)}{\mathrm{d}t} = \frac{h_D A_{ga}}{v_g}\left[c_{ff}(t) - \frac{c_g(t)}{K_{ga}}\right] \qquad (11)$$

We now have three coupled differential equations (6, 8, and 11) which can be solved for the concentration of aroma in the headspace, $c_g(t)$, according to the method of Laplace transforms. In Appendix A we show that the solution is

$$c_g(t) = \frac{A_{ga} h_D c_{tf}(0)}{v_g}\left[\mu U + \frac{V}{1 + K_b c_b}\right] \qquad (12)$$

where

$$U = \frac{s_1[1 - \exp(-s_2 t)] - s_2[1 - \exp(-s_1 t)]}{s_1 s_2 (s_1 - s_2)} \qquad (13)$$

$$V = \frac{\exp(-s_1 t) - \exp(-s_2 t)}{s_2 - s_1} \qquad (14)$$

and where

$$s_1 = \frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4\beta}}{2} \qquad (15)$$

and

$$s_2 = \frac{\alpha}{2} - \frac{\sqrt{\alpha^2 - 4\beta}}{2} \qquad (16)$$

with

$$\alpha = \frac{A_{ga} h_D}{v_a} + \frac{A_{ga} h_D}{v_g K_{ga}} + \mu + \lambda c_b \qquad (17)$$

and

$$\beta = \frac{A_{ga} h_D \mu}{v_a} + \frac{A_{ga} h_D}{v_g K_{ga}}(\mu + \lambda c_b) \qquad (18)$$

In eq 12 $c_{ff}(0)$ has been replaced using eq 4.

At long times, $t \to \infty$, the gas phase will become saturated with flavor and equilibrium conditions will be reached. The final headspace concentration is then given by

$$c_g(\infty) = \frac{c_{tf}(0)}{\dfrac{1 + K_b c_b}{K_{ga}} + \dfrac{v_g}{v_a}} \qquad (19)$$

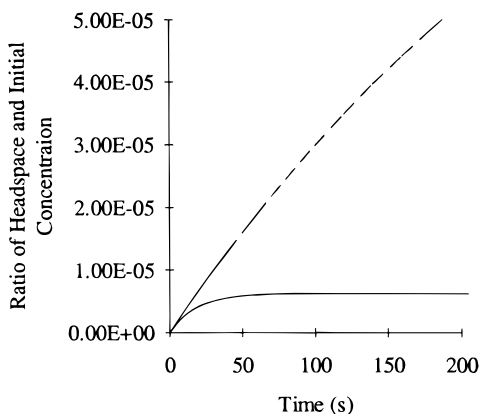**1886** *J. Agric. Food Chem.,* Vol. 45, No. 5, 1997

Harrison and Hills



**Figure 3.** Time-dependent flavor release curves for diacetyl (solid line) and heptan-2-one (dashed line). Here the mass transfer coefficient, $h_D$, is $5 \times 10^{-6}$ m/s. The polymer concentration, $c_{tb}$, is 10% and possesses a binding constant of 500 for both diacetyl and heptan-2-one.
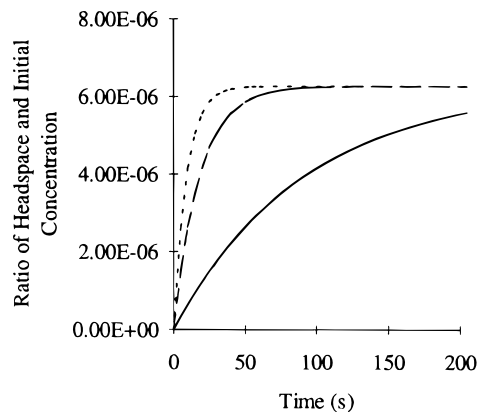


**Figure 4.** Time-dependent flavor release curves for diacetyl as a function of the mass transfer coefficient: solid line, $h_D = 1 \times 10^{-7}$ m/s; dashed line, $h_D = 5 \times 10^{-7}$ m/s; dotted line, $h_D = 1 \times 10^{-6}$ m/s. The polymer concentration, $c_{tb}$, is 10% and possesses a binding constant of 500.

It is very unlikely, however, that an aqueous mixture would reside in the mouth long enough for equilibrium conditions to be attained. We are therefore concerned with flavor release over short time scales. At short times, $t \rightarrow 0$, the exponential terms in eq 12 can be expanded to first order and predict a linear time dependence:

$$c_g(t) = \frac{h_D A_{ga}}{v_g} \frac{c_{tf}(0)}{1 + K_b c_b} t \qquad (20)$$

Equation 20 shows that for a fixed total flavor concentration the only influence on release at short times is through the variation of $h_D$, $K_b$, and $c_b$. The presence of the binder simply reduces the free flavor available for release by a factor of $(1 + K_b c_b)$, the same factor by which the partition coefficient is reduced. It is interesting to note that eq 20 also predicts that the initial release rate is independent of the gas–liquid partition coefficient and the rate constants $\lambda$ and $\mu$. At first this result may seem surprising; however, a similar result was obtained in previous work dealing with flavor release from liquid emulsions (Harrison *et al.*, 1997; Harrison and Hills, 1997) and is a consequence of the fact that the initial release depends only on the amount of free flavor already present in the liquid phase. Clearly this is not the case at longer times when the exact eq 12 must be used. In the next section we attempt to elucidate the main factors controlling flavor release from aqueous mixtures by examining the effects of $K_{ga}$, $h_D$, $K_b$, $c_b$, and the rate constants on the release profiles.

**Effect of Varying the Partition Coefficients.** Figure 3 shows the time-dependent release profiles of two volatiles, diacetyl and heptan-2-one. In this calculation we have assumed a mass transfer coefficient, $h_D$, of $2.5 \times 10^{-7}$ m/s, a binder concentration, $c_{tb}$, of 10%, and a polymer possessing a binding constant, $K_b$, of 500 for both volatiles. At short times the rates of flavor release for the two volatiles are identical in accordance with eq 20. At longer times diacetyl is more easily retained than heptan-2-one due to the differences in their hydrophobicity, which is reflected in their differing partition coefficients. We now turn to the other major factor controlling flavor release: the mass transfer coefficient, $h_D$.

**Effect of Varying the Mass Transfer Coefficient.** Figure 4 shows the effect of varying the interfacial mass

transfer coefficient, $h_D$, on the time-dependent flavor release profiles of diacetyl with all other parameters fixed: here $c_{tb}$ and $K_b$ assumed the values of 10% and 500, respectively. Figure 4 clearly shows that increasing $h_D$ results in faster rates of flavor release from liquid mixtures, as predicted by eq 20. Furthermore, Figure 4 demonstrates that $h_D$ does not influence the total amount of flavor released, which is instead controlled by the quantity of free flavor available, as predicted by eq 19.

One factor that will have a large effect on the mass transfer coefficient is the viscosity. Increasing the concentration of binder will produce an increase in the viscosity of the liquid mixture, producing a greater resistance to mass transfer in the surface layers of the liquid phase. The extent to which the viscosity increases will be largely dependent on the particular polymers added to the solution. In the case of liquid emulsions $h_D$ decreases exponentially with increasing oil fraction (Harrison *et al.*, 1997). In this paper we are concerned with the binding aspects of the added polymers, and therefore the viscosity dependence of $h_D$ will no longer be considered.

**Effect of Varying the Rate Constants.** As the free flavor is depleted from the aqueous phase fast exchange between the bound and unbound states will be required to replenish the free flavor available for release into the headspace. At short times eq 20 predicts that the rate constants $\mu$ and $\lambda$ do not influence the rate of release. In fact, our calculations show no evidence, even at longer times, to suggest that the dissociation of the polymer–volatile complex is ever the rate-limiting step, even when the dissociation was slow in comparison to partitioning into the headspace. At first sight this result may seem surprising, but it is a consequence of the extremely small amount of flavor released into the headspace compared with the amount of free flavor retained in the aqueous phase and predicted by eq 5 in the equilibrium state.

This suggests that a dependence on $\lambda$ and $\mu$ may be observed if the system were to start initially in a nonequilibrium state, where, for example, all of the flavor is initially bound in a polymer–volatile complex. Figure 5 shows that this is indeed the case, but only for very small values of the rate constants. At larger rate constants the rate-limiting step for flavor release is no longer the rate of flavor complex dissociation but the mass transfer across the gas mixture interface. This
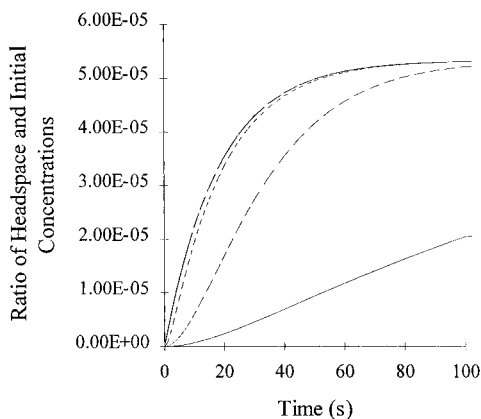
Flavor Release from Liquids Containing Aroma-Binding Polymers

*J. Agric. Food Chem.,* Vol. 45, No. 5, 1997 **1887**



**Figure 5.** Time-dependent flavor release curves for diacetyl as a function of the rate constant, $k_1$, when the volatile is initially completely in the bound state: solid line, $k_1 = 1 \times 10^{-3}$ m/s; dashed line, $k_1 = 1 \times 10^{-2}$ m/s; dotted line, $k_1 = 1 \times 10^{-1}$ m/s; dot-dashed line, $k_1 = 1$ m/s. The polymer concentration, $c_{tb}$, is 10% and possesses a binding constant of 500.

result is important in the consideration of flavor release in the mouth, where solids first have to be mixed with saliva to dissolve the polymer−volatile complex before dissociation and interfacial transfer into the headspace can occur. In this more complicated situation it is conceivable that the rate of ingredient−flavor dissociation may become rate limiting. This multistep process is outside the scope of the present paper and will be the subject of future investigations.

As the present work concerns only flavor release from aqueous solutions, we no longer need to consider the rate constants when predicting which factors control flavor release. Instead, we can assume the polymer−aroma interaction is always at equilibrium and write

$$c_{bf}(t) = K_b c_b c_{ff}(t) \qquad (21)$$

By differentiating eq 21 and substituting it into the equation for mass conservation (eq 11), we obtain

$$v_g \frac{dc_g(t)}{dt} + v_a(1 + K_b c_b)\frac{dc_{ff}(t)}{dt} = 0 \qquad (22)$$

Once the flavor is free in the aqueous phase, it is available for release into the headspace and can be described by the penetration theory of mass transfer, given by eq 11. In Appendix B we show, again by the method of Laplace transforms, that the solution to the two coupled differential equations (eqs 11 and 22) is

$$c_g(t) = \frac{c_{tf}(0)}{(1 + K_b c_b)/(K_{ga} + v_g/v_a)}\Bigg[1 - $$

$$\exp\Bigg[-\frac{A_{ga}h_D}{v_g}\Bigg(\frac{1}{K_{ga}} + \frac{v_g}{v_a}\frac{1}{1 + K_b c_b}\Bigg)t\Bigg]\Bigg] \qquad (23)$$

The final equilibrium flavor concentration in the headspace is obtained when $t \to \infty$ and is given by

$$c_g(\infty) = \frac{c_{tf}(0)}{\dfrac{1 + K_b c_b}{K_{ga}} + \dfrac{v_g}{v_a}} \qquad (24)$$

As expected, this result is identical to that obtained by considering explicitly the exchange of flavors between the bound and free states (eq 19). Furthermore, at short
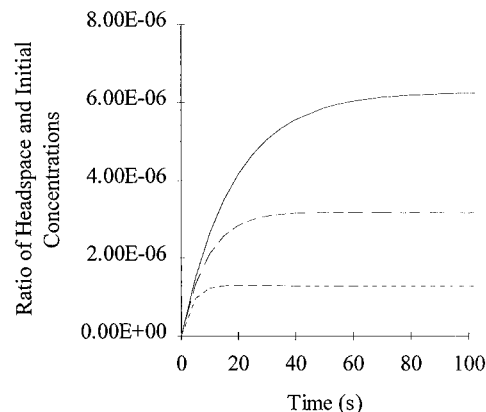


**Figure 6.** Time-dependent flavor release curves for diacetyl from liquid mixtures containing 10% (solid line), 20% (dashed line), and 50% (dotted line) of a binding polymer that possesses a binding constant of 500.
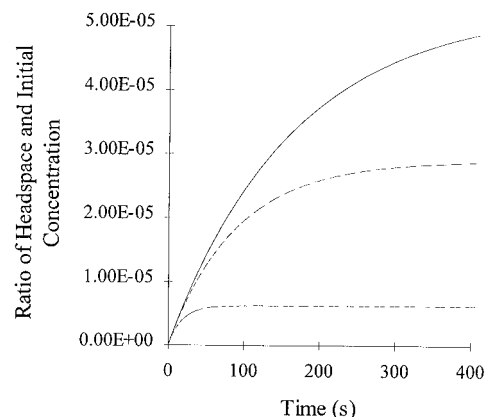


**Figure 7.** Time-dependent flavor release curves for diacetyl from liquid mixtures containing 10% of a binding polymer that possesses binding constants of 50 (solid line), 100 (dashed line), and 500 (dotted line).

times, *i.e.* $t \to 0$, the exponential term in eq 23 can be expanded to first order and predicts a linear time dependence

$$c_g(t) = \frac{h_D A_{ga}}{v_g}\frac{c_{tf}(t)}{1 + K_b c_b} \qquad (25)$$

which is again identical to the result obtained using the previous theory (eq 20) and confirms that, provided the initial liquid phase is at equilibrium, the initial release rate is independent of the absolute magnitudes of $\mu$ and $\lambda$ and depends linearly on the initial free flavor concentration. We will now examine the effects of the binding constant, $K_b$, and the binder concentration, $c_b$, on the time-dependent flavor release profiles.

**Effect of Varying the Binding Constant and Concentration.** Figure 6 shows the effect of the binder concentration on the release of diacetyl from an liquid mixture containing concentrations of 10%, 20%, and 50% binder. In this calculation we have assumed a binding constant of 500. As expected, when the binding concentration is increased, the quantity of flavor released into the headspace is greatly reduced. The initial rate of release is, however, is very similar for all three binder concentrations. Figure 7 also shows the release of diacetyl from an liquid mixture containing binding polymers but this time as a function of the binding constant. Here we have assumed a mass transfer coefficient of $5 \times 10^{-6}$ m/s and that the liquid mixture

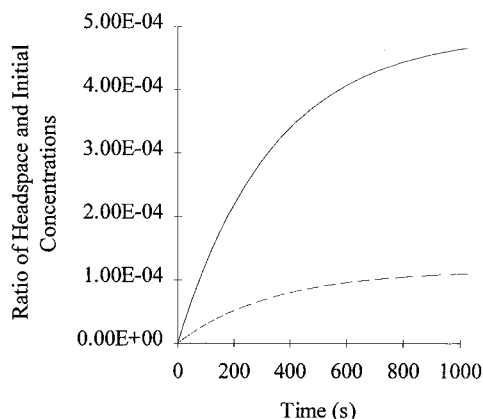**1888** *J. Agric. Food Chem.,* Vol. 45, No. 5, 1997

Harrison and Hills



**Figure 8.** Time-dependent flavor release curves for heptan-2-one from liquid mixtures containing soy protein (solid line) and BSA (dashed line).

contains 10% of a binding polymer. The results are similar to that of Figure 6, in that the quantity of volatile released into the headspace decreases with an increasing binding constant, *i.e.* with the polymer's increasing ability to bind a greater quantity of volatile. Again the initial release rates are very similar for all three binder concentrations.

The next step is to test the theory with real data for a real system whose partition coefficients and binding constants are known. A good example may be the release of heptan-2-one from aqueous solutions containing 10% of either soy protein or bovine serum albumin (BSA), for which the binding constants are 110 and 500, respectively (Kinsella, 1989). We have made some predictions for this system using a gas–water partition coefficient for 2-heptanone, $K_{ga}$, equal to $5.9 \times 10^{-3}$ (Kinsella, 1989) and assuming a mass transfer coefficient of $5 \times 10^{-6}$ m/s for both calculations (Figure 8). It should be noted, however, that in reality the mass transfer coefficient will vary between liquid mixtures, and only experiment can determine the true values of $h_D$. Figure 8 predicts that heptan-2-one should be more readily released into the headspace from aqueous solutions containing soy protein than BSA, which reflects the smaller binding constant for soy protein. This example also serves to illustrate how replacing one polymer by another changes the binding characteristics of the liquid mixture and hence alters the flavor release profiles. In this way knowledge of the binding properties between volatiles and ingredients could be extremely useful in the formulation of the flavor of new liquid food products.

## CONCLUSIONS

In this paper we have presented a mathematical model that describes the release of volatiles into a closed headspace from aqueous solutions containing polymers which reversibly bind to volatiles. The presence of binding polymers in the solutions reduces the quantity of free flavor available for release and hence flavor perception. The model is based on two main assumptions: first, the transport of volatiles across the gas–liquid interface can be described by the penetration theory of interfacial mass transfer; and second, the rate of exchange of volatiles between the bound and unbound states is always at equilibrium and can be described by first-order chemical kinetics.

Somewhat surprisingly, our results show that the rate constants describing the exchange of volatiles from the

bound to unbound states do not influence the release profiles and hence are not rate limiting. This is found to be a consequence of the large quantity of free flavor initially present in the aqueous phase, and hence available for release, and, the very small quantity of flavor required to partition into the closed headspace in comparison to the large amount of free flavor initially available in the solution.

Our theory shows that the main effect of adding binding polymers to an aqueous solution is to reduce the free flavor available for release and to alter the interfacial mass transfer coefficient. At short times, relevant to flavor release in the mouth, eq 20 predicts that the rate of flavor release is affected by the binding constant, $K_b$, but that the most important factor affecting flavor release, at short times, is the mass transfer coefficient, which will depend greatly on the viscosity of the liquid mixture and hence the type of polymer introduced. At present the relative importance of these factors can only be determined experimentally and this highlights the need for careful measurements of the relevant partition coefficients, mass transfer coefficients, and binding constants.

The model suggests that dissociation of a polymer–aroma complex could become rate limiting if all of the aroma is initially complexed in a (semi-) solid complex, which then has to dissolve in saliva to form a solution. In this situation either the breakdown of the (semi-) solid food matrix or the chemical dissociation step could be rate limiting. Theories for the effect of the matrix breakdown have already been formulated (Hills and Harrison, 1995; Harrison and Hills, 1996). The next, and more complicated, step is to incorporate chemical binding into these models, which will be the subject of future work.

## APPENDIX A

First, we take Laplace transforms of eq 6 of the main text to yield

$$sc_{ff}(s) - c_{ff}(0) = \mu c_{bf}(s) - \lambda c_b c_{ff}(s) + \frac{s v_g c_g(s)}{v_a} \quad (A1)$$

where $c_{ff}(0)$ is the initial free flavor. Here it has been assumed that the initial flavor in the headspace, $c_g(0)$, is zero. Rearranging eq A1 for $c_{bf}(t)$ gives

$$c_{bf}(s) = \frac{1}{\mu}\left[ c_{ff}(s)(s + \lambda c_b) + \frac{s v_g c_g(s)}{v_a} - c_{ff}(0)\right] \quad (A2)$$

Second, we take Laplace transforms of eq 8 to yield

$$v_g s c_g(s) = -v_a[s c_{ff}(s) - c_{ff}(0) + s c_{bf}(s) - c_{bf}(0)] \quad (A3)$$

Again it is assumed that $c_g(0)$ is equal to zero. Substitution of eq A2 into eq A3 and rearranging gives

$$c_g(s)\left[v_g s + \frac{v_g s^2}{\mu}\right] + c_{ff}(s)\left[v_a s + \frac{v_a s(s + \lambda)}{\mu}\right] = v_a\left[c_{tf}(0) + \frac{s}{\mu}c_{ff}(0)\right] \quad (A4)$$

which can be written in the form

$$e c_g(s) + f c_{ff}(s) = v_a\left[c_{tf}(0) + \frac{s}{\mu}c_{ff}(0)\right] \quad (A5)$$

Flavor Release from Liquids Containing Aroma-Binding Polymers

*J. Agric. Food Chem.,* Vol. 45, No. 5, 1997  **1889**

where

$$e = v_g s + (v_g s^2/\mu) \tag{A6}$$

and

$$f = v_a s + [v_a s(s + \lambda)/\mu] \tag{A7}$$

And finally, taking Laplace transforms of eq 11 yields

$$sc_g(s) - c_g(0) = \frac{h_D A_{ga}}{v_g}\left[c_{ff}(s) - \frac{c_g(s)}{K_{ga}}\right] \tag{A8}$$

which can be rearranged to give

$$c_g(s)[v_g s + (h_D A_{ga}/K_{ga})] + c_{ff}(s)[-h_D A_{ga}] = 0 \tag{A9}$$

Here we have assumed that the initial concentration of flavor in the gas phase is zero, *i.e.* $c_g(t{=}0) = 0$. Equation A9 can be written in the form

$$gc_g(s) + hc_{ff}(s) = 0 \tag{A10}$$

where

$$g = v_g s + (h_D A_{ga}/K_{ga}) \tag{A11}$$

and

$$h = -h_D A_{ga} \tag{A12}$$

The first step to obtaining a solution for the time dependence of $c_g(t)$ is to write eqs A5 and A10 as simultaneous equations in matrix form

$$\mathbf{A}\begin{pmatrix} c_g(s) \\ c_{ff}(s) \end{pmatrix} = \begin{pmatrix} v_a c_{tf}(t) + sv_a c_{ff}(0)/\mu \\ 0 \end{pmatrix} \tag{A13}$$

where $\mathbf{A}$ is given by

$$\mathbf{A} = \begin{pmatrix} e & f \\ g & h \end{pmatrix} \tag{A14}$$

Multiplying both sides of eq A13 by $\mathbf{A}^{-1}$, the inverse matrix of eq A14, gives

$$\begin{pmatrix} c_g(s) \\ c_{ff}(s) \end{pmatrix} = \mathbf{A}^{-1}\begin{pmatrix} v_a c_{tf}(0) + sv_a c_{ff}(0)/\mu \\ 0 \end{pmatrix} \tag{A15}$$

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

$$c_g(s) = \frac{h}{\det \mathbf{A}}\left[v_a c_{tf}(0) + \frac{sv_a c_{ff}(0)}{\mu}\right] \tag{A16}$$

where $h$ is given by eq A12 and $\det \mathbf{A}$ by

$$\det \mathbf{A} = -\left(\frac{v_g v_a}{\mu}\right)(s^3 + \alpha s^2 + \beta s) \tag{A17}$$

where

$$\alpha = \frac{A_{ga}h_D}{v_a} + \frac{A_{ga}h_D}{v_g K_{ga}} + \mu + \lambda c_b \tag{A18}$$

and

$$\beta = \frac{A_{ga}h_D \mu}{v_a} + \frac{A_{ga}h_D}{v_g K_{ga}}(\mu + \lambda c_b) \tag{A19}$$

Equation A17 can be written in the form

$$\det \mathbf{A} = -(v_a v_g/\mu)s(s + s_1)(s + s_2) \tag{A20}$$

where the roots are given by the quadratic formula

$$s_1 = \frac{\alpha}{2} + \frac{\sqrt{\alpha^2 - 4\beta}}{2} \tag{A21}$$

and

$$s_2 = \frac{\alpha}{2} - \frac{\sqrt{\alpha^2 - 4\beta}}{2} \tag{A22}$$

The expression for the determinant (eq A20) can now be substituted into eq A16 to give

$$c_g(s) = \frac{A_{ga}h_D}{v_g}\left[\frac{\mu c_{tf}(0)}{s(s + s_1)(s + s_2)} + \frac{c_{ff}(0)}{(s + s_1)(s + s_2)}\right] \tag{A23}$$

The inverse Laplace transforms of eq A23 is eq 12 in the main text.

APPENDIX B

Taking Laplace transforms of eq 22 in the main text and rearranging for $c_{ff}(s)$ gives

$$c_{ff}(s) = \frac{c_{ff}(0)}{s} - \frac{v_g}{v_a}\frac{c_g(s)}{1 + K_b c_b} \tag{B1}$$

Substituting eq B1 into eq A9 from Appendix A and rearranging for $c_g(s)$ produces

$$c_g(s) = \frac{A_{ga}h_D c_{ff}(0)}{v_g}\frac{1}{s(s + T)} \tag{B2}$$

where

$$T = \frac{A_{ga}h_D}{v_g}\left(\frac{1}{K_{ga}} + \frac{v_g}{v_a}\frac{1}{1 + K_b c_b}\right) \tag{B3}$$

The inverse Laplace transforms of eq B2 is eq 23 in the main text.

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**1890** *J. Agric. Food Chem.,* Vol. 45, No. 5, 1997

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