Kinetic Origin of Tailing in Chromatography

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▶ **Tailing may be assumed to originate as a kinetic phenomenon when the sorption isotherm is linear. The various mechanisms for this are discussed. Equations are then presented for an idealized model for tailing, first proposed by Giddings and Eyring in 1955. Concentration profiles are obtained and plotted for both elution and nonelution chromatography. Tailing may originate when a sorption site exists which holds molecules for a time equal to that necessary for one quarter of the zone to pass by. In gas liquid chromatography this is equivalent to having a small percentage of the stationary liquid in pores with seven to eight times the normal diffusion distance.**

TAILING in chromatography may appear as anything from a slight zone asymmetry up to a severe zone distortion with a considerable mass of material stringing out behind the bulk of the zone. Most zones are at least slightly affected by this phenomenon. The harmful effects of tailing are in rough proportion to the excess spreading of the zone rearward, a spreading which can overlap or mask other zones.

Tailing is usually blamed on a nonlinear adsorption isotherm. This is rather natural, because the earliest theories of chromatography (*3, 13*), showed that nonlinear adsorption isotherms were sources of very high asymmetry. Recent work with ultrasensitive detectors in gas chromatography has shown, however, that tailing often exists when solute concentrations are well below the point where a noticeable departure from linearity occurs. It is thus necessary to explain certain occurrences of tailing in terms of a linear picture of chromatography.

The first explanation for tailing in the presence of linear sorption was apparently given by Giddings and Eyring in 1955 (*7*). A kinetic mechanism, in which adsorption occurs on two types of sites, was postulated. It was assumed that the second type of site, with a high adsorption energy, was relatively scarce. Molecules would not often be "captured" by such a site, but when adsorption did occur the molecules would be held for a considerable time. When desorption finally occurred, the bulk of the zone would already have passed over. Desorption would thus occur into the trailing part of the zone and the resulting buildup of concentration would appear as a tailing phenomenon. We may call this kind of site a "tail-producing site."

Keller and Giddings (*10*) have calculated concentration profiles for zones which are influenced by a slow, reversible chemical reaction between chromatographic migrants. Such a reaction may occur between isomers, etc., as migration proceeds. The resulting profiles frequently show tailing (as well as "fronting"). It was thus demonstrated that tailing may have a kinetic origin even in the presence of a linear isotherm.

A qualitative discussion of tailing in capillary gas liquid chromatography has been given by Golay (*8*). The assumed mechanism is the absorption and holdup of solute molecules in excess droplets of liquid. This concept is apparently the same as that proposed by Giddings and Eyring, except that the slowness of desorption is caused by an excessive diffusion distance rather than by a high-energy adsorption site.

Another source of tailing in the linear range is the presence of excess dead volume in the system, usually in the injection or detection units. The explanation is much like the others given above: A quantity of solute can be shunted into dead pockets, where a sufficient time elapses before it escapes to cause tailing. Johnson and Stross (*9*) have shown tailing profiles which originate with a large detector volume within which perfect mixing is assumed.

No other mechanism in the linear range has been postulated which would give a significant degree of tailing [a normal elution profile will always show a slight positive skew (*7*), but for narrow zones this is not significant]. In the nonlinear range, of no direct interest here, a number of mechanisms for tailing have been proposed. These include the effect of the adsorption isotherm, volume changes caused by sorption (*1*), and temperature changes caused by sorption (*6, 12*).

THEORY

The theory given here will implement the original suggestion by Giddings and Eyring. Although a two-site theory has been extensively developed (*5, 7, 11*), it is too difficult to apply in rigorous form, particularly when a more attractive alternative exists. As shown by Keller and Giddings (*10*), the fast exchange reaction (as on the first or "normal" type of site) leads to an effective diffusion process whose spreading influence can be readily calculated. This is superimposed on the effect of the slow exchange process on the tail-producing site. The latter must be calculated by rigorous theory.

It will be assumed that the first-order adsorption and desorption rate constants on the tail-producing site are k_a and k_d, respectively. Thus $1/k_a$ will be the mean time required for a molecule to adsorb on this type of site and $1/k_d$ will be the mean time required for a molecule, once adsorbed, to detach itself. It will further be assumed that all of the solute is in the mobile phase as migration begins.

Elution Development. It has been shown (*7*) that the elution profile corresponding to the above assumptions is

$$P(t_s) = \left(\frac{k_a k_d t_m}{t_s}\right)^{1/2} e^{-k_a t_m - k_d t_s} I_1\left(\sqrt{4 k_a k_d t_m t_s}\right) \quad (1)$$

where t_s is the (variable) time spent adsorbed on the tail-producing site, and is thus the time measured from the appearance of a normal peak—i.e., a peak undisturbed by slow adsorption. An inert peak (the "air" peak in gas chromatography) requires a fixed time, t_m, to migrate through the column. The quantity $I_1(X)$ is a Bessel function of imaginary argument.

Equation 1 is more conveniently written in terms of the reduced time variable, y, where $y = t_s/t_m$. The dimensionless parameters, a_1 and a_2, are equal to $k_a t_m$ and $k_d t_m$, respectively. With this change of terms and variables Equation 1 becomes

$$P(y) = \left(\frac{a_1 a_2}{y}\right)^{1/2} e^{-a_1 - a_2 y} I_1\left(\sqrt{4 a_1 a_2 y}\right) \quad (2)$$

The molecules which escape through the column without ever being adsorbed on those sites are not allowed for in Equation 2. These molecules appear as a narrow pulse at time $t_s = 0$ and the ideal profile contributed by them, analogous to Equation 2, is

$$P'(y) = e^{-a_1}\,\delta(y) \quad (3)$$

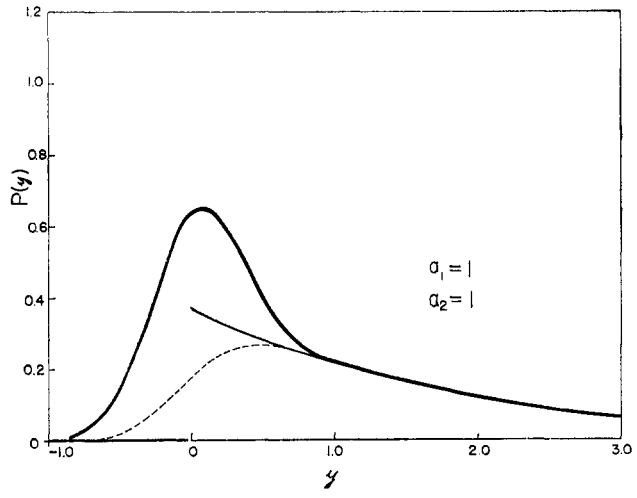

Figure 1. Elution profile with $a_1 = 1$ and $a_2 = 1$

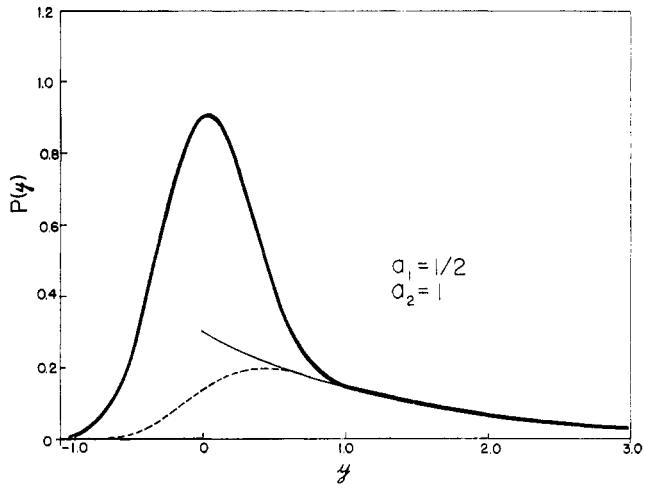

Figure 2. Elution profile with $a_2 = 1/2$ and $a_1 = 1$

In this and subsequent profiles the light solid line is a direct consequence of the tail-producing sites, the dashed line is the same except as it is smeared by column processes, and the heavy solid line is the final concentration profile

where the delta function, $\delta(y)$, signifies an infinitely thin pulse at $y = 0$. The addition of Equations 2 and 3 yields a concentration profile normalized to unit area. This undisturbed profile must now be modified to allow for the effective diffusion processes of the column. This is a simple matter for that part of the concentration profile found in Equation 3, since a Gaussian profile is found immediately. A numerical procedure must be used for $P(y)$. The Schmidt method (*2*) has been used for this purpose here. The degree of effective diffusion which will occur will be related to the number, N, of theoretical plates in the column (excluding the effects of second-site adsorption). This is discussed below.

t_s is the time measured from the appearance of the center of the undisturbed chromatographic peak. This peak will, however, require a time t (the elution time) after injection to make its appearance. Thus our coordinate systems using t_s or y have their origins a time t after injection.

The effective diffusion of solute is related to both t and the number, N, of plates in the column. Thus the standard deviation, τ, on the time scale (which may be used as the parameter-characterizing diffusion) is given by $\tau = t/\sqrt{N} = (t_m/\sqrt{N})(t/t_m)$. The ratio t_m/t is simply the R value (zone velocity over carrier velocity) for the undisturbed component peak. Thus $\tau = t_m/R\sqrt{N}$. The standard deviation, σ_y, along the y axis is given by $\sigma_y = \tau/t_m$. Thus

$$\sigma_y = 1/R\sqrt{N} \qquad (4)$$

Thus if one chooses reasonable values for R and N, the diffusion parameter, σ_y, is determined and the calculations can be made accordingly.

Nonelution Chromatography. The nonelution or on-column zone profile resulting from slow second-site kinetics is given by the sum of the following equations (*10*).

$$P_3(x) = b \exp[-a(1-x) - bx] \; I_0\sqrt{4abx(1-x)} \qquad (5)$$

$$P_4(x) = [abx/(1-x)]^{1/2} \exp[-a(1-x) - bx] \; I_1\sqrt{4abx(1-x)} \qquad (6)$$

$$P_5(x) = e^{-b}\,\delta(1) \qquad (7)$$

where x is the fraction of the total time, t, spent unattached to the second site and thus $1 - x$ is the fraction of time spent adsorbed on this type of site. Since the molecule is migrating normally when unattached, x may be thought of as a reduced distance coordinate representing the distance traveled relative to that of the undisturbed zone. The zone profile calculated from these equations will, then, simply represent the distribution of component along the column length, $x = 0$ and 1 being the initial and final positions of the undisturbed zone, respectively.

The kinetic parameters of Equations 5, 6, and 7 are $a = k_d t$ and $b = k_a R t$ (the R appears in the last expression because only the fraction R of unattached molecules is free to react, the rest being adsorbed on the normal sites). Both I_0 and I_1 are Bessel functions.

The effective diffusion processes of the column, to be superimposed on the profile discussed above, is once again related to the number of plates generated in migrating to the final position a distance L along the column. The standard deviation, σ, developed by an undisturbed zone, is given by $L/\sqrt{N}$ in this case. The standard deviation in x, σ_x, is modified to σ/L because of the change in scale factor. Thus

$$\sigma_x = 1/\sqrt{N} \qquad (8)$$

Once N is fixed at a reasonable value, the extent of diffusion can be calculated in accordance with the σ_x obtained.

RESULTS

Calculations have been made which indicate the degree of tailing caused by slow sorption-desorption processes. The computed profiles are shown in Figures 1 to 6.

Elution Chromatography. Figures 1 to 4 pertain to elution chromatography. Different kinetic parameters, a_1 and a_2, are used in the calculations, but the columns from which these profiles might be expected are otherwise assumed to be identical. Except for the disturbance which leads to tailing, each column is assumed to have a thousand plates, $N = 1000$, and the R value is assumed to be 0.1. A change in these values would alter the details of the profiles but the main features would be unchanged.

Each figure consists of three curves. The curve with the sharp discontinuity at $y = 0$ is that calculated from Equation 2 for those molecules which are captured at least once by the second kind of site. The dotted line is the profile obtained from this through a diffusion process corresponding to 1000 plates (Equation 4). The heavy line is the final profile, a sum of the dotted line and the Gaussian resulting from the diffusion of the spike in Equation 3.

The zero on the y scale corresponds to the emergence of the undisturbed peak. Since y is a measure of time in units of the dead time, t_m, and since $R = 0.1$, the initial injection occurs at $y = -10$

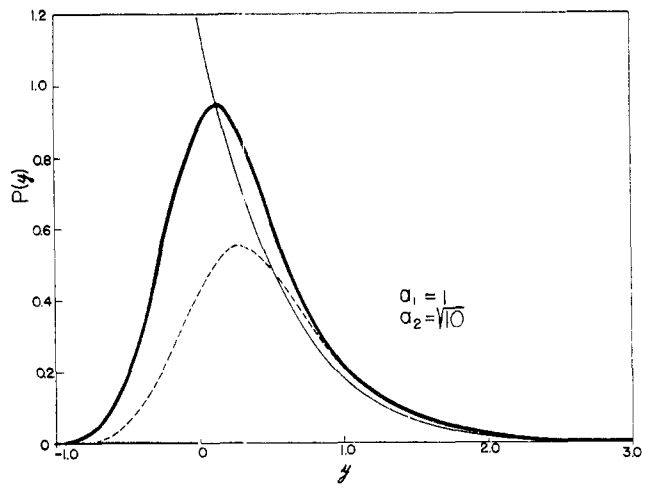

Figure 3. Elution profile with $a_1 = 1$ and $a_2 = \sqrt{10}$

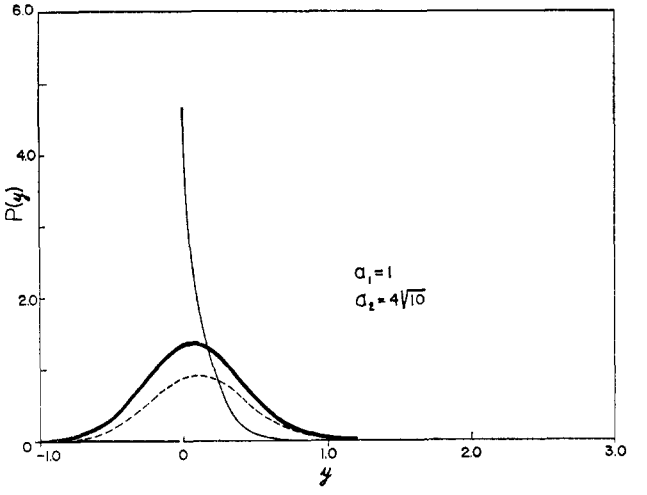

Figure 4. Elution profile with $a_1 = 1$ and $a_2 = 4\sqrt{10}$

for all these cases. This fact gives some perspective to the type of chromatograph this column would yield.

Figure 1 shows a very significant degree of tailing. This profile is calculated with $a_1 = a_2 = 1$. These parameters, interpreted simply, mean that 63% of the molecules become attached at least once to the tail-producing site and that 37% of the molecules pass through the column without attachment. A molecule, once attached, requires a mean time t_m for desorption. It is this slowness of desorption which produces tailing, for in the time a molecule remains attached to this site an inert peak passes through the entire column length. This explains why the tail in Figure 1 is spread out over several y units, each y unit being the passage time of the inert peak. In this same time of attachment the bulk of the component zone migrates through $^1/_{10}$ (since $R = 0.1$) of the column length. Since at its widest point (just before elution) the zone width, 4σ, is only $^1/_8$ of the column length, a molecule lost to a tail-producing site from the center of the zone will not ordinarily emerge again until the zone is well past. It is molecules of this sort which form a tail by desorbing to the rear of the zone.

Figure 2 is similar to Figure 1. The only difference is that a_1 has been changed from 1 to $^1/_2$. This means that more molecules (61% instead of 37%) migrate through the column without being disturbed by the tail-producing sites. The concentration in the tail (controlled by a_1) is thus less, but its length (controlled by a_2) is just as great.

In Figure 3 a_2 has been increased from 1 to $\sqrt{10}$. This increase in desorption rate reduces the length of the tail. The tailing is still noticeable, however. The value $\sqrt{10}$ was chosen for a_2 in order to make k_d equal $1/\tau$, where τ is the standard deviation of the undisturbed peak in time units just before its elution. The fact that k_d equals $1/\tau$ can be shown by writing $k_d = a_2/t_m = \sqrt{10}/t_m$, and $1/\tau = R\sqrt{N}/t_m = \sqrt{10}/t_m$. If a different column with some other N is chosen, we would expect a similar profile as long as $k_d = 1/\tau$, an equality that can be arranged by letting $a_2 = R\sqrt{N}$.

Figure 4 shows a profile in which a_2 has been increased to $4\sqrt{10}$—i.e., $k_d = 4/\tau$. Very little tailing is evident. This was anticipated, since a molecule held up by a tenacious site for the time $1/k_d$, or $\tau/4$, desorbs again before a very large fraction of the zone has gone by. Figures 3 and 4 taken together show that as a rough rule tailing is not a major concern unless $k_d \leq 1/\tau$ or $a_2 \leq \sqrt{N}/R$.

Magnitude of Rate Constant for Tail-Producing Sites. Throughout this paper we have emphasized the wide difference existing between tail-producing sites and normal sites. It is worth calculating the extent of that difference in at least one limiting case.

If zone spreading in the undisturbed zone is controlled by adsorption and desorption on the normal sites (rather than by longitudinal diffusion, etc.), the column plate height is (4)

$$H = 2R(1 - R)v/k_d' \qquad (9)$$

where v is the mean velocity of the mobile phase and k_d' is the rate constant for desorption from the normal site. Since $a_2 = k_d t_m$, the ratio of k_d' to k_d is

$$k_d'/k_d = 2R(1 - R)N/a_2 \qquad (10)$$

where N has been used in place of L/H. The critical value of a_2, from above, is $R\sqrt{N}$, which combined with Equation 10 gives

$$k_d'/k_d = 2(1 - R)\sqrt{N} \qquad (11)$$

Thus for the parameters used in this paper, $N = 1000$ and $R = 0.1$, the tail-producing site must have a desorption rate some 58 times slower than normal in order to be significant. If factors other than adsorption-desorption rates control the plate height, the discrepancy would need to be even greater.

Application to Gas Liquid Chromatography. Some degree of tailing is encountered in most applications of gas liquid chromatography in spite of the fact that ultrasensitive ionization detectors have led to an ever-decreasing sample size. Assuming that this tailing may often have a kinetic origin, we can postulate two mechanisms which may be responsible. First a few active sites on the solid support may lead to tailing. All active adsorption sites, it should be emphasized, will not lead to tailing under linear conditions, but only those which succeed in retarding solute for a time comparable to τ, as discussed above.

The second mechanism for tailing may originate in liquid diffusion. The units of liquid which cause retention are distributed in a complex geometrical way, presumably with a wide variation in physical dimensions. Any unit of liquid held in, say, a long narrow pore will equilibrate slowly with external solute because of the large effective diffusion distance, d. The equilibration time increases with d^2 and thus the effective desorption constant, k_d, is proportional to $1/d^2$. (Even though desorption is no longer a single-step process, the essential nature of desorption is little changed.) Thus if one is looking for a pool of liquid which will produce tailing, and which must therefore have a k_d value 58 or so times smaller than average, one finds that the effective diffusion distance must be seven to eight times the normal distance. The relative amount of stationary phase which must be tied up in these abnor-

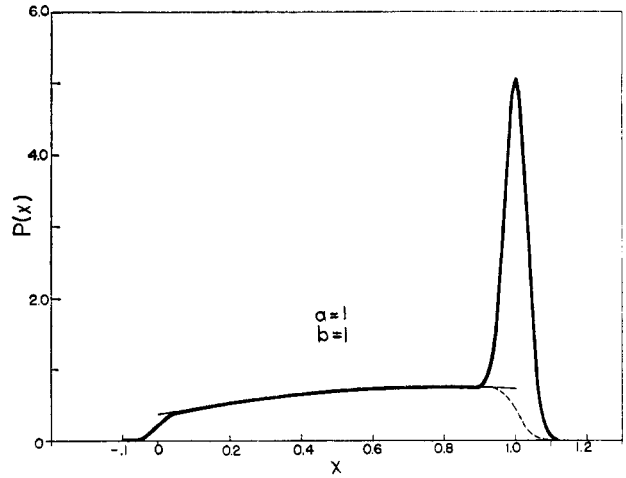

Figure 5. Nonelution profile with $a = 1$ and $b = 1$

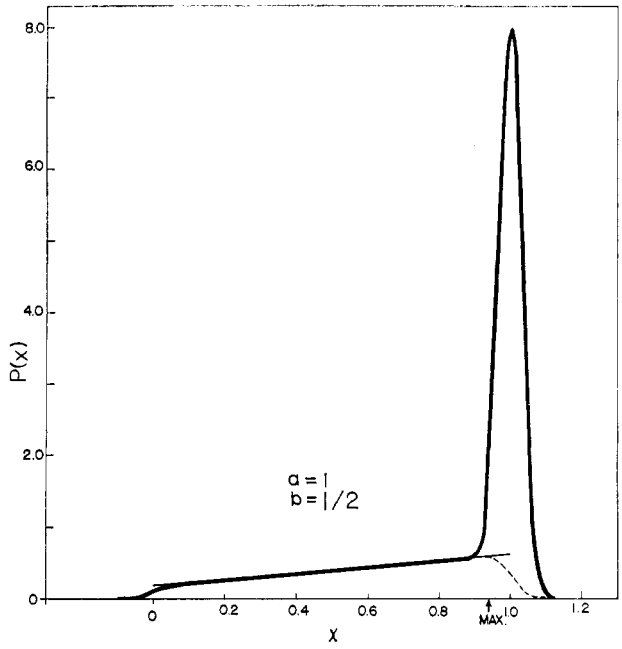

Figure 6. Nonelution profile with $a = 1$ and $b = 1/2$

mally large units is the additional retention time, τ, caused by these units divided by the normal retention time, t, minus t_m. This fraction is $1/(1 - R)\sqrt{N}$. For the parameters used above this is 0.035—i.e., 3.5% of the liquid should be found in large units. This requirement could probably be relaxed somewhat, since tailing would undoubtedly be discernable if a_1 were several times less than the value used in Figure 3. Probably 1 to 2% liquid would suffice. The nature of such liquid—whether it occurs in elongated pores, caverns with restricted entry, or large units formed from small ones running together—is highly uncertain at this point.

Nonelution Chromatography. Figures 5 and 6 show concentration profiles for nonelution chromatography. Once again a column is assumed which generates 1000 plates and the R value is 0.1. Figure 5 is plotted with the parameters $a = 1$ and $b = 1$. The tailing is more prominent than in Figure 5 where the sorption rate is cut in half, $b = 1/2$, and a remains at unity. The gross features of these profiles are very similar to those for elution. Also in common with the elution case, the tail will hold up longer when the desorption rate parameter, a, is small, and contain more material when the sorption rate parameter, b, is large. The only significant difference between elution and nonelution cases lies in the termination of the tail; the elution tail diminishes gradually to zero, while the nonelution tail (for the parameters used here) is cut off rather sharply at the origin of migration. In paper chromatography a very weak spot may be left at the origin. This is presumably due to adsorption taking place before development is started, a case not covered in the equations given here.

CONCLUSIONS

Tailing can originate as a kinetic effect even with a linear isotherm. It is not clear how often this occurs. One of the objects of the present work is to define the nature of the kinetic effect so that it can be more readily identified in experimental work. Two main points distinguish the kinetic effect from other effects, particularly nonlinear ones:

Nonlinear tailing will decrease as the sample size is lowered, whereas kinetic tailing will be little affected by such changes.

Kinetic tailing will be especially prominent at high velocities. If one takes two zones of equal width at half height, one at a selected high velocity where rate effects dominate and another at a low velocity where longitudinal diffusion effects are of equal magnitude, the high-velocity zone will show more tailing. Nonlinear tailing will show little difference.

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