Influence of Mixing State of Carrier Fluid in Nonlinear Equilibrium Exchange Systems

It is shown that for a given residence time distribution of carrier fluid and a given nonlinear adsorption isotherm of a single solute, the breakthrough curve is not uniquely defined. The special case of a one-dimensional dispersive flow is examined. It is shown that with a simple but realistic model for the residence time distribution, the classical self-sharpening front becomes a continuously broadening front. Two extreme models are proposed to describe the behavior of any front in a flow system with a given residence time distribution. This study seems of crucial importance in systems for which this residence time distribution is the only available information about the flow pattern.

D. SCHWEICH

Laboratoire des Sciences du Genie
Chimique
CNRS-ENSIC
Nancy, France

SCOPE

A step composition change performed at the inlet of an equilibrium exchange system may lead to two kinds of elution curves: 1) a continuously broadening front due to the conjugated effects of dispersion and nonlinear isotherm; and 2) a profile of constant pattern or shock layer due to the balanced effects of dispersion and nonlinear isotherm. For a Langmuir isotherm the second situation is observed when the solute saturates the column, the first situation when a desaturation front propagates. The special case of the constant pattern behavior has been studied by Rhee et al. (1970), Cooney and Lightfoot (1965), and Vermeulen et al. (1973). All their theories and results are deduced from the classical model of the one-dimensional convective and dispersive flow based on Fick's law.

One of the aims of this paper is to show that their results and especially the asymptotic constant shape of the front for a saturation front is due to their particular choice of the flow model. If the only available information about the flow pattern in the equilibrium exchange system is the residence time distribution (RTD) several alternate models may be used to model the flow and the following question arises: For a given RTD looking like the RTD of a convective and dispersive flow, is the constant pattern profile always observed? We shall see that the answer is no. This is of crucial importance for example in hydrofogy for which the RTD is often the only available information about the flow pattern. In the more familiar exchange systems encountered in chemical engineering, many results and published papers rely on the assumption that a self-sharpening front must occur for a saturation with a favorable isotherm: Coppola and Levan (1981) studied the effects of the boundary conditions used with the dispersion equation for an accurate prediction of the front. Helfferich (1970) has shown that the classical formula for the height equivalent to a theoretical plate (HETP) as derived from the theory of linear chromatography is only applicable to trace solutes if they obey a nonlinear adsorption law. All these "classical" results will be reconsidered in the light of the choice of the model for the RTD when the only broadening process is the dispersion one.

The concepts described in this paper are very similar to those of micromixing phenomena studied by Zwittering (1959). His two extreme models for a given RTD will be used to described the transient nonlinear adsorption together with the classical mixing cells in series model (Wen and Fan 1975, Villermaux 1981, 1982). It will be shown that the broadening of the front depends upon the model.

CONCLUSIONS AND SIGNIFICANCE

Assuming that the RTD of the exchange system is known and looks like the RTD of a convective and dispersive flow, the saturation front of a solute obeying a Langmuir adsorption law is studied according to the choice of the model for the given RTD. With the model based on Fick's law the well-known asymptotic and constant shape is obtained. If the RTD is the result of independent flow trajectories in parallel in which the dispersion process does not occur the situation is dramatically different: the front continuously broadens as it does in linear chromatography. Moreover this front propagates as a front of solute obeying a linear isotherm which is the chord to the actual nonlinear isotherm extending from the composition before the saturation to the composition after the saturation. By analogy with Zwittering's work, this kind of flow is called a segregated nondispersive (SND) flow. The Zwittering's concept of maximum mixedness (MM) is introduced and it is shown that: 1) a saturation front in the maximum mixed state is steeper than the front obtained with the mixing cells model which is itself steeper than the front obtained in a SND flow; and 2) a desaturation front in a SND flow is steeper than the front obtained with the mixing cells model which is again steeper than the front obtained in the maximum mixedness state. The differences between the fronts are especially noticeable in the case of the so-called self-sharpening front which becomes "self-broadening" in the SND flow. This new result may explain the lack of conclusive experiments to our knowledge which would illustrate quantitatively the properties of a profile of constant pattern. Finally, by analogy with the work of Zwittering, it may be supposed that the fronts obtained in a SND flow and in the MM state are the two extreme situations between which an experimental curve will lie. It is thus proposed to study the actual shape of this curve to have further insight in the flow pattern behavior.

INTRODUCTION

In his historic paper, Zwittering (1959) has explained the effect of the mixing state of the fluid on the yield of a reaction carried out in a given reactor. When the kinetic reaction rate is nonlinear, he has shown that the conversion of a key reactant is not uniquely defined by the residence time distribution (RTD). The goal of this paper is to show a similar effect in nonlinear transient adsorption

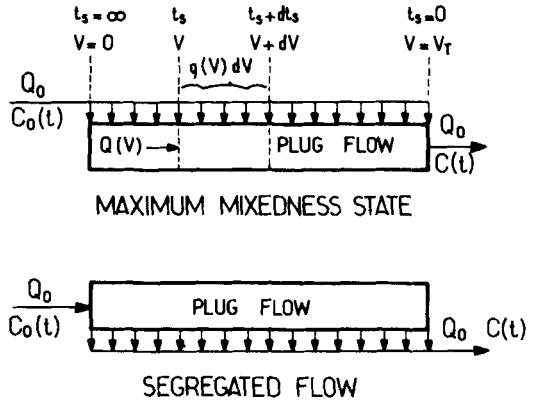

Figure 1. Zwittering's two models for mixing state of a fluid. The RTD is obtained by a suitable distribution of the outlet or inlet.

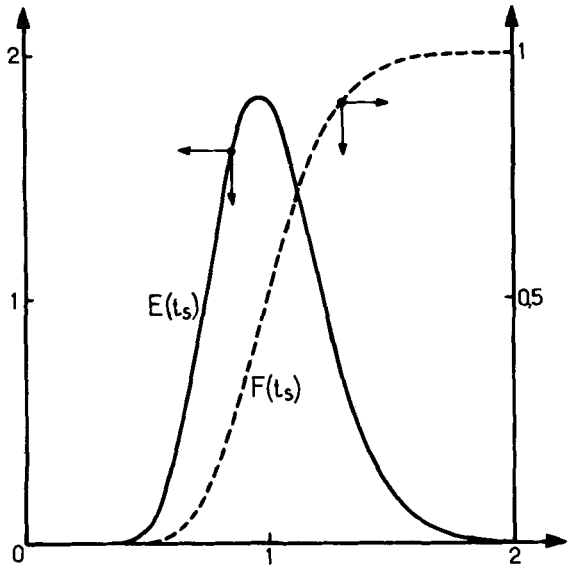

Figure 2. Residence time distribution (continuous curve) and integrated residence time distribution (dotted curve) for a one-dimensional dispersive flow (conditions given by Eq. 11).

since in many flow systems the only available information on the flow pattern is the RTD. For example, in hydrology a RTD measurement allows a simple description of a natural flow of water between two wells though this flow may be the result of a complicated velocity field.

To take into account the mixing state of the fluid, Zwittering considered two simple flow patterns giving the same RTD. They consist of either a distributed inlet or distributed outlet along the axis of an ideal plug-flow reactor (Figure 1). The first case is the state of maximum mixedness (MM) of the fluid, the second case is the completely segregated flow. The RTD is obtained by a suitable distribution of the flow rate along the axis. Zwittering has shown that the distribution is the same in the two cases.

Now let us suppose that a solute obeying a Langmuir adsorption law is injected in a one-dimensional dispersive flow. Cooney and Lightfoot (1965), Rhee et al. (1970), Vermeulen et al. (1973), and Coppola and Levan (1981) have shown that a saturation front reaches an asymptotic shape when dispersion is the only broadening process. In other words, the broadening of the front does not increase continuously with the volume or the mean residence time of the exchange system. Let us show that, for the given RTD of the dispersive flow, this result is a consequence of a particular model for the mixing state of the fluid. If the same saturation front is injected in the segregated flow of Figure 1, it propagates as a sharp discontinuity inside the tube where there is no dispersion (Helfferich and Klein, 1970). In this situation the broadening of the outlet

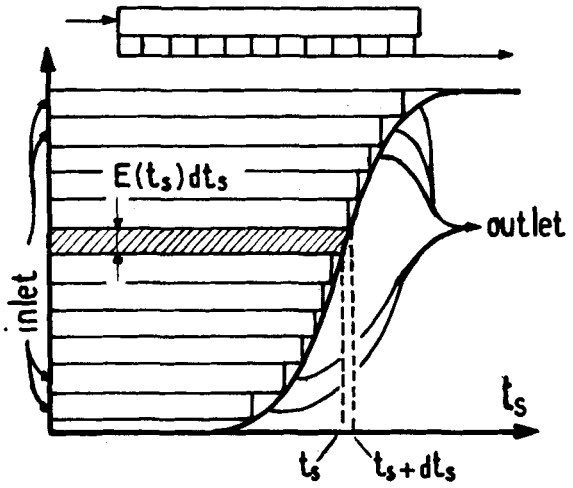

Figure 3. Model of parallel streamlines for segregated nondispersive flow. The residence time is given by Figure 2.

front is only due to the mixing of the distributed outlet streams. It occurs after the propagation process and not simultaneously. As a consequence, the sharpening behavior of the front does not balance the dispersion process and the front continuously broadens as the mean residence time increases.

This shows that according to the mixing state of the fluid, the same RTD may lead either to a self-sharpening or a self-broadening front. This observation, immediately obvious when stated, has never appeared before.

To analyze the importance of this effect, we shall describe the mathematical models for the transient adsorption process in the two extreme mixing states, Figure 1. For the sake of simplicity we shall focus our attention on RTD which is similar to the RTD given in Figure 2. It will be represented by the RTD of J mixing cells in series (Wen and Fan, 1975; Villermaux, 1981, 1982). If t_o is the mean residence time of the fluid it is:

$$E(t_s) = \left(\frac{J}{t_o}\right)^J t_s{}^{J-1} \frac{e^{-Jt_s/t_o}}{(J-1)!} \tag{1}$$

J accounts for axial dispersion. The larger J, the weaker the dispersion process. From a chromatographic point of view, J is the number of theoretical plates of the column when no mass transfer limitation occurs. Though it is the special case of a convective and dispersive one-dimensional flow, the method and the results described below remain valid for any other RTD. The adsorbable solute will be assumed to follow a Langmuir adsorption law:

$$n = \frac{NKC}{1 + KC} \tag{2}$$

EQUILIBRIUM EXCHANGE IN A SEGREGATED NONDISPERSIVE FLOW

Let us assume that a front of solute propagates in the segregated flow, Figure 1. We shall say that the front propagates in a segregated nondispersive (SND) flow. A simple image of this kind of flow is given by the model of the bundle of parallel streamlines (Olson and Stout, 1967; Villermaux, 1974, 1982), Figure 3. The exchange system is supposed to be composed of many parallel and independent tubes. To create the RTD, a given tube with the residence time t_s is fed with the fraction $Q_oE(t_s)dt_s$ of the total volumetric flow rate Q_o. The response of this given tube to an arbitrary injection of solute is a function $f(t,t_s)$. The response of the overall system is the sum of the responses of each tube weighted by the fraction of flow rate:

$$C(t) = \int_o^\infty f(t,t_s)E(t_s)dt_s \tag{3}$$

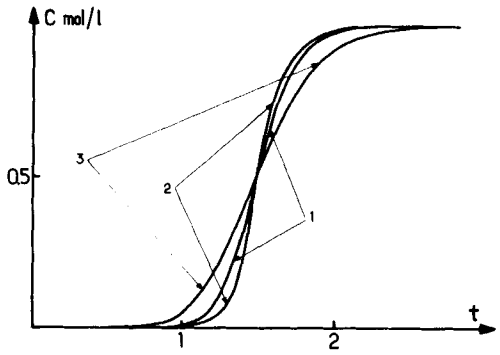

Figure 4. Behavior of a saturation front of a solute which obeys a Langmuir adsorption law: 1) mixing cells in series; 2) maximum mixedness state; 3) segregated nondispersive flow. The difference between the fronts is due to the choice of the model for the given RTD of Figure 2. Though these curves are called self-sharpening fronts, curve 3 always broadens.

When the function $f(t,t_s)$ is known, Eq. 3 allows the front in the SND flow to be computed. A special case is given by unit front of an unretained solute:

$$f(t,t_s) = H(t - t_s) \tag{4}$$

Where H stands for the heaviside step function. Equations 3 and 4 give:

$$C(t) = \int_o^\infty H(t - t_s)E(t_s)dt_s = \int_o^t E(t_s)dt_s = F(t) \tag{5}$$

Where $F(t)$ is the integrated RTD (IRTD), Figure 2. Examine the behavior of a saturation front of an adsorbable solute. In a nondispersive flow Helfferich and Klein (1970), and Aris and Amundson (1973) have shown that the front propagates as a sharp discontinuity. If u is the velocity of the carrier fluid, ν the volume ratio of solid to fluid, the velocity of the front in an empty column is:

$$v = \frac{u}{1 + \nu \dfrac{n_o}{C_o}} \tag{6}$$

where C_o is the magnitude of the front. In the tube of residence time t_s, the front appears when:

$$t = t_s \frac{u}{v} = t_s \left(1 + \nu \frac{n_o}{C_o}\right) \tag{7}$$

Thus, $f(t,t_s)$ is given by:

$$f(t,t_s) = C_o H\left(t \frac{v}{u} - t_s\right) = C_o H\left[\frac{t}{1 + \nu \dfrac{n_o}{C_o}} - t_s\right] \tag{8}$$

Equations 3 and 8 give:

$$C(t) = C_o \int_o^\infty H\left[\frac{t}{1 - \nu \dfrac{n_o}{C_o}} - t_s\right] E(t_s)dt_s$$

$$= C_o F\left(\frac{t}{1 + \nu \dfrac{n_o}{C_o}}\right) \tag{9}$$

Equation 9 shows that a saturation front in a SND flow is given by the IRTD and the slope (n_o/C_o) of the chord to the nonlinear isotherm extending from $C = 0$ to $C = C_o$. Between these concentration limits the above equations, especially Eq. 9, are valid whatever the shape of the isotherm. For the linear isotherm:

$$n = C \frac{n_o}{C_o} \tag{10}$$

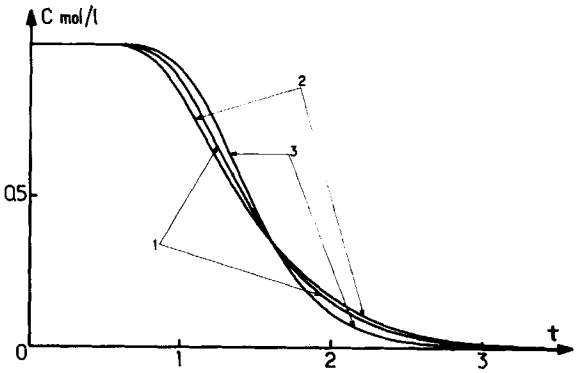

Figure 5. Same as Figure 4, but for a desaturation front.

It is well known that the front continuously broadens as long as it propagates in the exchange system. Since Eq. 9 holds for both linear and nonlinear adsorption this implies that a "self-sharpening" front of a solute obeying a nonlinear isotherm does not reach an asymptotic shape and behaves as a linear front in a SND flow. As a consequence, the classical formulas for the height equivalent to a theoretical plate (HETP), as derived by many authors in the case of linear chromatography (Giddings, 1965; Villermaux, 1981), remain valid in the SND flow though Helfferich and Klein (1970) have said that they are restricted to trace solutes.

The curve 3 of Figure 4 illustrates the saturation front in the SND flow for the following conditions:

$$\begin{array}{llll} J = 20 & t_o = \text{unit of time} & C_o = 1 \text{ mol/L} \\ \nu = 1 & N = 1 \text{ mol/L} & K = 1 \text{ L/mol} \end{array} \tag{11}$$

These values are chosen as an illustrative example. They reflect a highly dispersive flow and a moderately nonlinear isotherm.

Equation 3 allows the desaturation front to be computed. In this situation the function $f(t,t_s)$ is the equation for the front in a nondispersive flow. It is derived in appendix from the results of Aris and Amundson (1973). With the values of the parameters given in Eq. 11, it leads to the curve 3 of Figure 5.

EQUILIBRIUM EXCHANGE IN MAXIMUM MIXEDNESS STATE

To show the influence of the mixing state of the fluid, we shall now describe the behavior of the same fronts of solute in the flow system of Figure 1 which illustrates the maximum mixed (MM) state. Figure 1 shows the notation which will be used in the mass balance equations. Let us first calculate the distribution density $q(V)$ of the lateral feed flow rate. The residence time of carrier fluid fed at the abscissa V is:

$$t_s = \int_V^{V_t} \frac{dV}{Q(V)} \quad \text{or } dt_s = -\frac{dV}{Q(V)} \tag{12}$$

Where $Q(V)$ is the volumetric flow rate inside the tube at the abscissa V and V_t the total volume of fluid phase. The fraction of carrier fluid the residence time of which lies between t_s and $t_s + dt_s$ is thus:

$$E(t_s)dt_s = -\frac{q(V)}{Q_o}dV = \left\{\begin{matrix}\text{fraction of fluid} \\ \text{fed in } dV\end{matrix}\right\} \tag{13}$$

When the RTD is given, Eqs. 12 and 13 allow to calculate $q(V)$:

$$q(V)\frac{Q(V)}{Q_o} = E(t_s); \quad \frac{Q(V)}{Q_o} = \int_o^v \frac{q(V)}{Q_o}dV \tag{14}$$

$$Q(V) = Q_o[1 - F(t_s)]; \quad q(V) = \frac{E(t_s)}{1 - F(t_s)} \tag{15}$$

The mass balance equation for an adsorbable solute in the system of Figure 1 is:

$$qC_o(t) = qC(t,V) + Q\frac{\partial C}{\partial V} + \frac{\partial C}{\partial t} + \nu\frac{\partial n}{\partial t} \tag{16}$$

With Eq. 13, the volume V is eliminated from Eq. 16 and we get:

$$\frac{E(t_s)}{1-F(t_s)}[C(t,t_s)-C_o(t)]-\frac{\partial C}{\partial t_s}+\frac{\partial C}{\partial t}+\nu\frac{\partial n}{\partial t}=0 \quad (17)$$

Equation 17 describes the behavior of the front of solute $C_o(t)$ in an exchange system in the MM state with the *RTD* $E(t_s)$. The solution $C(t,t_s)$ for $t_s = 0$ is the equation for the outlet front. The proper boundary condition which is required to solve Eq. 17 has been discussed by Zwittering (1959) and Villermaux (1970). At the beginning of the reactor of Figure 1 we have from Eq. 12:

$$t_s = \infty \quad V = 0 \quad (18)$$

Nevertheless, the concentration $C(t,t_s)$ must be bounded at this singular point. This implies:

$$\frac{\partial C}{\partial t_s} \to 0 \text{ when } t_s \to \infty \quad (19)$$

With the chosen RTD (Eq. 1) it may be shown that (see appendix):

$$\frac{E(t_s)}{1-F(t_s)} \to J/t_o \text{ when } t_s \to \infty \quad (20)$$

Let $\overline{C}(t)$ be the limit value of $C(t,t_s)$ when t_s goes to infinity. From Eqs. 17, 19 and 20, $\overline{C}(t)$ is the solution of:

$$\frac{J}{t_o}[\overline{C}(t)-C_o(t)]+\frac{\partial \overline{C}}{\partial t}+\nu\frac{\partial \overline{n}}{\partial t}=0 \quad (21)$$

Equation 21 allows the boundary condition $\overline{C}(t)$ required by Eq. 17 when t_s goes to infinity to be computed. The integration procedure of Eqs. 17 and 21 is briefly outlined in the Appendix. In the conditions given by Eq. 11 it leads to the curves 2 of Figures 4 and 5. It is easily seen that the fronts are different according to the mixing state of the fluid though the RTD and the adsorption law are identical.

DIRECT SOLUTION OF MASS BALANCE EQUATIONS

The curves 1 in Figures 4 and 5 show the fronts calculated by direct integration of the mass balance equations for the mixing cells in series (Appendix). Once more the curves are different but they are located "between" the curves for SND flow and the MM state.

DISCUSSION

The above results show that the broadening behavior of a front of an adsorbable solute depends on the mixing state of the fluid. As a consequence, it becomes necessary to know which mixing state is the closest to the real operating conditions of an exchange system.

1) In a chromatographic column the self-sharpening behavior of a saturation front is easily observed. This implies that SND flow is unrealistic. In properly packed columns, the radial dispersion, either by diffusion or by convective dispersion with a particle Peclet number of about 10 will prevent the independence of the parallel tubes of Figure 3. The MM state is probably the best description of the situation.

2) In chemical reaction engineering the effect of the mixing state of the fluid on the yield of a reaction has been extensively studied. It is commonly assumed that any experimental result will lie between the two limits given by the two flow patterns proposed by Zwittering. Though no clear demonstration has been given, no experimental proof of the contrary is available. By analogy, it may be thought that any experimental front will be located between those calculated in the SND flow and the MM state. This is already the case for the fronts deduced from the model of the mixing cells in series.

3) Large-scale systems with a nonuniform flow cannot be described by the SND flow or the MM state. The actual mixing state of the fluid lies between these limits and have to be modeled by a suitable sequence of distributed outlets and inlets along the axis of the plug-flow system (Villermaux, 1974). Nevertheless, from the above remark, the front due to an intermediate mixing state would lie between the fronts due to the SND flow and the MM state. As a consequence, our approach would allow computing the two fronts between which any experimental curve would be located. This may be useful, for example, in evironmental systems where the determination of flow patterns is either impossible or very expensive.

4) It is a matter of straightforward (but tedious) calculation to show that, whatever the mixing state, the fronts are identical when the solute obeys a linear isotherm. Our approach is thus useful only when the absorption process has nonlinear behavior.

Apart from these practical implications, several questions arise from the above theoretical results:

1) If all fronts are supposed to lie between the fronts due to the SND flow and the MM state, we must include the asymptotic front of Cooney and Lightfoot, Rhee et al., and Vermeulen et al. Since the saturation front in the SND flow continuously broadens, the front in the MM state must be steeper than the asymptotic front and at least it cannot broaden. Has the saturation front in the MM state a constant shape or does it shrink as the mean residence time or the volume of the flow system increases?

2) Chemical reactions involving nonlinear reaction rates are used to investigate the micromixing phenomena. Could the study of an experimental breakthrough curve of a solute obeying a known nonlinear adsorption law be a method for studying the flow pattern in an exchange system?

3) Throughout this paper it has been assumed that the only nonthermodynamic broadening process is due to dispersion. Our results cannot be used when mass transfer limitations occur. Nevertheless, Eqs. 3 and 17 could be adapted to this new situation. It is important to know whether our results are drastically changed or not.

4) It must be kept in mind that the first studies of the micromixing phenomenon show slight effects on the yield of simple reactions. It is now well known that these effects may be large for competing reactions or highly nonlinear reaction rates (Zoulallian and Villermaux, 1974; Plasari et al., 1978; Klein et al., 1980). Consequently, if the effect shown on Figures 4 and 5 is slight it may become larger either in other physical conditions or with other adsorption laws. This shows that the single numerical example given in Figures 4 and 5 is not sufficient to prove the usefulness of our approach and that experimental evidence of the phenomenon or further theoretical investigations are necessary.

ACKNOWLEDGMENTS

J. Villermaux, D. Tondeur, and J. A. Dodds are gratefully acknowledged for the time spent in useful discussions on this subject.

APPENDIX: COMPUTATION OF THE FRONTS

1) For the saturation front in the SND flow, Eq. 9 is used.

2) For the desaturation front in the SND flow, with the results of Aris and Amundson (1973) the following equations are obtained:

$$f(t,t_s) = 0 \quad \text{when } t > t_s(1+\nu NK) \quad (A1)$$

$$f(t,t_s) = C_o \quad \text{when } t < \left(1+\frac{\nu NK}{(1+KC_o)^2}\right) \quad (A2)$$

$$f(t,t_s) = \frac{1}{K}\left[\sqrt{\frac{\nu NKt_s}{t-t_s}}-1\right] \quad \text{when } t < t_s(1+\nu NK) \text{ and } t > t_s\left(1+\frac{\nu NK}{(1+KC_o)^2}\right) \quad (A3)$$

Numerically with conditions 11:

$$f(t,t_s) = 0 \quad \text{when } t > 2t_s \tag{A4}$$

$$f(t,t_s) = 1 \quad \text{when } t < 5t_s/4 \tag{A5}$$

$$f(t,t_s) = \left[\sqrt{\frac{t_s}{t-t_s}} - 1\right] \quad \text{when } 5t_s/4 < t < 2t_s \tag{A6}$$

Finally:

$$C(t) = \int_{t/2}^{4t/5} \left[\sqrt{\frac{t_s}{t-t_s}} - 1\right] E(t_s)dt_s + \int_{4t/5}^{\infty} E(t_s)dt_s \tag{A7}$$

Since $E(t_s)$ is a normalized function we have:

$$C(t) = \int_{t/2}^{4t/5} \left[\sqrt{\frac{t_s}{t-t_s}} - 1\right] E(t_s)dt_s + 1 - \int_{o}^{4t/5} E(t_s)dt_s \tag{A8}$$

Equation A8 is used to compute curve 3 of Figure 5.

3) For the saturation front in the MM state, the first problem is the calculation of the boundary condition $\overline{C}(t)$. For a saturation front, Eq. 21 reduces to:

$$\frac{J}{t_o}\left[\overline{C}(t) - C_o\right] + \frac{\partial \overline{C}}{\partial t} + \nu \frac{\partial \overline{n}}{\partial t} = 0 \tag{A9}$$

$$\overline{C}(o) = 0$$

Straightforward calculation shows that the solution of Eq. A9 is:

$$J\frac{t}{t_o} = \left[1 + \frac{\nu NK}{(1+KC_o)^2}\right] Ln\left(\frac{C_o}{C_o - \overline{C}}\right) + \frac{\nu NK}{(1+KC_o)^2} Ln\,(1+K\overline{C}) + \frac{\nu NK}{1+KC_o}\frac{K\overline{C}}{1+K\overline{C}} \tag{A10}$$

Secondly, Eq. 17 is numerically integrated (Runge-Kutta). To avoid the singular point $t_s = \infty$, the new variable $\theta = t_o/(t_o + t_s)$ is used. Equation 17 becomes:

$$\frac{E\left(t_o\frac{1-\theta}{\theta}\right)}{1 - F\left(t_o\frac{1-\theta}{\theta}\right)}[C - C_o] + \frac{1}{t_o\theta^2}\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial t} + \nu\frac{\partial n}{\partial t} = 0 \tag{A11}$$

Equation A11 is integrated from $\theta = 0$ ($t_s = \infty$) up to $\theta = 1$($t_s = 0$). $C(t, \theta = 1)$ is the equation for curve 2 of Figure 4.

4) For the desaturation front in the MM state, Eq. 21 becomes:

$$\frac{J}{t_o}\overline{C}(t) + \frac{\partial \overline{C}}{\partial t} + \nu\frac{\partial \overline{n}}{\partial t} = 0 \tag{A12}$$

$$\overline{C}(\mathrm{O}) = C_o$$

The solution is:

$$J\frac{t}{t_o} = (1 + \nu NK)\,Ln\left(\frac{C_o}{\overline{C}}\right) + \nu NK\,Ln\left(\frac{1+K\overline{C}}{1+KC_o}\right) + \nu NK\left[\frac{1}{1+KC_o} - \frac{1}{1+K\overline{C}}\right]$$

Then Eq. A11 is used.

5) For the mixing-cell model, the mass balance in cell number i is:

$$C_{i-1} = C_i + \frac{t_o}{J}\left[\frac{dC_i}{dt} + \nu\frac{dn_i}{dt}\right] \tag{A13}$$

The set of J Eq. A13 is integrated with the proper initial and boundary conditions:

Saturation:	$C_o(t) = C_o$	$C_i(\mathrm{O}) = 0$	$i = 1$ to J
Desaturation:	$C_o(t) = 0$	$C_i(\mathrm{O}) = C_o$	$i = 1$ to J

$C_J(t)$ is the equation for curves 1 in Figures 4 and 5.

6) For the derivation of Eq. 2, we have:

$$E(t_s) = \left(\frac{J}{t_o}\right)^J t_s{}^{J-1}\frac{e^{-Jt_s/t_o}}{(J-1)!} \tag{A14}$$

$$1 - F(t_s) = \int_{t_s}^{\infty} E(u)du = e^{-Jt_s/t_o}\sum_{n=0}^{J-1}\frac{(Jt_s/t_o)^n}{n!} \tag{A15}$$

From Eqs. A14 and A15 we have:

$$\frac{E(t_s)}{1-F(t_s)} = \frac{J}{t_o}\frac{(Jt_s/t_o)^{J-1}/(J-1)!}{\sum_{n=0}^{J-1}(Jt_s/t_o)^n/n!} \tag{A16}$$

and

$$\frac{E(\infty)}{1-F(\infty)} = \frac{J}{t_o} \tag{A17}$$

NOTATION

C = concentration in mobile phase (mol/L)
C_o = concentration in feed (mol/L)
$E(t_s)$ = residence time distribution
$f(t,t_s)$ = equation for a front deduced from equilibrium theory of chromatography
$F(t_s)$ = integrated residence time distribution
J = number of mixing cells
K = Langmuir's isotherm parameter (L/mol)
n = concentration in stationary phase (mol/L)
N = limiting value of n (mol/L)
q = flow rate distribution
Q,Q_o = integrated flow rate distribution, total flow rate
t = time
t_s = residence time
t_o = mean residence time of an unretained solute
V,V_T = volume of mobile phase, total volume of mobile phase

Greek Letters

ν = volume ratio of solid to fluid
θ = transformed residence time (see Appendix)

Subscripts

i = index of a cell in mixing cells model

LITERATURE CITED

Aris, R. and N. R. Amundson, Eds., *Mathematical Methods in Chemical Engineering*, **2**, Prentice-Hall (1973).

Cooney, D. O., and E. N. Lightfoot, "Existence of Asymptotic Solutions to Fixed-Bed Separations and Exchange Equations," *Ind. Eng. Chem. Fund.*, **4**, 233 (1965).

Coppola, A. P., and M. D. Levan, "Adsorption with Diffusion in Deep Beds," *Chem. Eng. Sci.*, **36**, 967 (1981).

Giddings, J. C., *Dynamics of Chromatography. Part I: Principles and Theory*, M. Dekker, New York (1965).

Helfferich, F., and G. Klein, Multicomponent Chromatography, Theory of Interference, *Chromat. Sci. Ser.*, **4**, M. Dekker (1970).

Klein, J. P., R. David, and J. Villermaux, "Interpretation of Experimental Liquid Phase Micromixing Phenomena in a Continuous Stirred Reactor with Short Residence Time," *Ind. Eng. Chem. Fund.*, **15**, 373 (1980).

Olson, J. H. and L. E. Stout, "Mixing and Chemical Reactions," *Mixing Theory and Practice*, Eds., V. W. Uhl, T. B. Gray, Academic Press, New York, **2**, 146 (1967).

Plasari, E., R. David, and J. Villermaux, "Micromixing Phenomena in Continuous Stirred Reactors Using a Michaelis-Menten Reaction in the Liquid Phase," *ACS Symp. Ser.*, **65**, 11 (1978).

Rhee, H. K., B. F. Bodin, and N. R. Amundson, "A Study of the Shock Layer in Equilibrium Exchange Systems," *Chem. Eng. Sci.*, **26**, 1571 (1971).

Vermeulen, T., G. Klein, and N. K. Heister, "Adsorption and Ion Exchange," *Chemical Engineer's Handbook*, 5th Ed., Eds., R. H. Perry and C. H. Chilton, McGraw Hill, New York (1973).

Villermaux, J., *Génie de la Réaction Chimique. Conception et Fonctionnement des Reacteurs*, Ed., Lavoisier, Technique et Documentation, Paris (1982).
Villermaux, J., "Theory of Linear Chromatography," *Percolation Processes: Theory and Applications*, Eds., A. Rodrigues and D. Tondeur, Sjthoff and Noordhoff, 1 (1981).
Villermaux, J., "Distribution des Temps de Séjour et Mélange Maximal par un Modèle de Mélangeurs en Cascade avec Alimentation Étagée," *Can. J. Chem. Eng.*, **48**, 317 (1970).
Villermaux, J., "Letter to the Editor," *Chem. Eng. Sci.*, **21**, 1054 (1974).
Wen, C. Y., and L. T. Fan, Eds. "Models for Flow Systems and Chemical Reactors," *Chemical Processing and Engineering*, **3**, M. Dekker (1975).
Zoulalian, A., and J. Villermaux, "Influence of Chemical Parameters on Micromixing in a Continuous Stirred Tank Reactor," *Adv. in Chem. Ser.*, **133**, 348 (1974).
Zwittering, T. W., "The Degree of Mixing in Continuous Flow Systems," *Chem. Eng. Sci.*, **11**, 1 (1959).

Manuscript received March 29, 1982; revision received November 30, and accepted December 14, 1982.

Kynch Theory and Compression Zones

BRYANT FITCH
Auburn University
1570 Oak St.
Napa, CA 94559

Kynch's theories of sedimentation are reinterpreted, modified, and extended to be valid for batch sedimentation in which a zone of compacting sediment forms at the bottom of the column. The development has several steps: First, it is shown that a concentration discontinuity, any part of whose chord plots above the curve on a Kynch plot of settling flux vs. particle concentration, will be unstable and immediately give rise to a different concentration distribution. From this it is deduced that Kynch characteristics, or loci of constant concentration, must propagate either from the origin of a height vs. time plot, or tangentially from the locus of the compression or suspension-sediment discontinuity. A Kynch-like construction is derived to relate the settling rate at the top of the suspension (measured by its subsidence rate) to the concentration arriving at the surface at that time. It makes use of two tangents, one to the settling curve (as in Kynch), and another to the locus of the compression discontinuity. Finally a construction, analagous to that of Talmage and Fitch, is deduced for determining required thickener area.

SCOPE

Kynch's well-known theory of sedimentation is based on the assumption or premise that the settling rate at any point in a column of suspension would be a function only of the concentration at that point; i.e., $u = u(c)$. He showed that, where his assumption is uniformly valid, "the relationship between settling rate and particle concentration can be deduced from observations on the fall of the top of the suspension" (in a batch test). But Kynch's assumption is not valid throughout a column in which a zone of compacting sediment forms at the bottom. In the compaction zone itself, u is not dependent on c alone, but also on the solids stress gradient (Michaels and Bolger, 1962; Fitch, 1966, 1975, 1979; Shirato et al., 1970). And just above the compaction zone, the Kynch zones or characteristics do not arise from the origin, as demanded by Kynch theory, but arise from the interface between the compacting sediment and the zone-settling suspension above it (Fitch 1966, 1969; Tiller, 1981). As a consequence, procedures for determining the unit area needed in a Dorr-type thickener, that are based on Kynch theory, are without theoretical basis. In particular, the Talmage and Fitch (1955) procedure for thickener design is unsound.

Tiller (1981) shows that Kynch theory can be corrected or extended to cover the case in which a subjacent compression zone is formed. This is done by taking into consideration the rise of the suspension-sediment interface, as well as the fall of the suspension-supernatant interface. Tiller's procedure, however, is complicated. It involves trial and error selection of a set of characteristic lines such that the integrated amount of solids crossing the suspension-sediment interface up to any time, plus the amount remaining in suspension at that time, equals the amount originally present in the suspension.

The Tiller paper does not recognize or make use of a relationship that follows from Kynch theory: Any characteristic that arises from the compression interface must do so tangentially. Use of this relationship makes it possible to replace the complicated Tiller procedure with a simple geometric construction. And corrections to the Talmage and Fitch construction can be derived.

CONCLUSIONS AND SIGNIFICANCE

Kynch's theory has been generalized and extended to account for the presence of a compaction zone at the bottom of a batch sedimentation column. Means have been given to deduce the relationship between settling rate u and particle concentration c, in the region for which $u = u(c)$, from observations on the fall of the top of the suspension and the rise of the compression interface. The rise of the compression interface, however, is not visible. It could in principle be observed with the aid of radiation absorption instruments. It can also be plotted from the observed compression points of a series of batch settling tests having the same concentration but different initial heights. The latter, however, requires multiple tests, which negates the principal practical advantage of Kynch-type procedures for specifying thickener unit area. The method would, therefore, seem to be of greater theoretical significance than of practical utility.