ChE laboratory

NEW ADSORPTION METHODS*

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ADSORPTION AND ION EXCHANGE systems are used for a variety of separations and purifications in industry. Many different operational techniques have been proposed for these separation schemes. In this review we will first develop a simple method (suitable for undergraduate and graduate students) for following the movement of a solute in an adsorption or ion exchange system. Then this solute movement will be used to study a variety of operational methods. Much of this paper appeared previously [23].

SOLUTE MOVEMENT

Consider first a bed of porous particles. The particles have an interparticle (between different particles) porosity of α and an intraparticle (within a given particle) porosity of ϵ. The total porosity of the bed for small molecules is $\alpha + (1-\alpha)\epsilon$. This is illustrated in Fig. 1. In addition, large solutes will not be able to penetrate all of the intraparticle void space. The fraction of volume of the particle which any species can penetrate is K_d. For a non-adsorbed species, K_d can be determined from

$$K_d = \frac{V_e - V_o}{V_i} \tag{1}$$

where V_e is the elution volume, V_o is the external void volume between the particles, and V_i is the internal void volume. When the molecules are small and can penetrate the entire interparticle volume, $V_e = V_i + V_o$ and $K_d = 1.0$. When the molecules are large and can penetrate none of the interparticle volume, $V_e = V_o$ and $K_d = 0$.

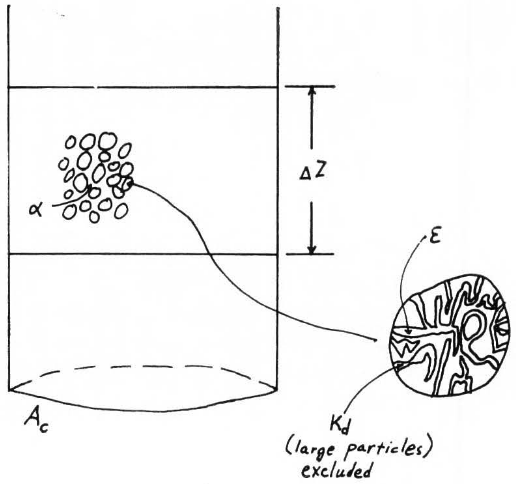

FIGURE 1. Porosities in packed bed.

As solutes migrate through the bed they can be in the mobile fluid in the external void volume, in the stagnant fluid inside a particle, or sorbed to the particle. The only solutes which are moving towards the column exit are those in the mobile fluid. Consider the movement of an incremental mass of solute added to a segment of the bed shown in Fig. 1. Within this segment this incremental amount of solute must distribute to form a change in fluid concentration, Δc, and a change in the amount of solute adsorbed, Δq. The amount of this increment of solute in the mobile fluid compared to the total amount of solute increment in this segment is

$$\frac{\text{Amt. in mobile fluid}}{\text{Total amt. in segment}} = \frac{\text{Amt. in mobile fluid}}{\text{Amt. in: (Mobile fluid + stationary fluid + sorbed)}} \tag{2}$$

which is

$$\frac{\text{Amt. in mobile fluid}}{\text{Total amt. in segment}} = \frac{(\Delta z A_c)\,\alpha\Delta c}{(\Delta z A_c)\,\alpha\Delta c + (\Delta z A_c)\,(1-\alpha)\,\epsilon\Delta c K_d + (\Delta z A_c)\,(1-\alpha)\,(1-\epsilon)\,\rho_s \Delta q K_d} \tag{3}$$

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The solid density, ρ_s, is included in Eq. (3) to make the units balance. A_c is the cross sectional area, and z is the axial distance.

If fluid has a constant interstitial velocity, v, then the average velocity of the solute in the bed (the solute wave velocity) is just v times (relative amount of time the incremental amount of solute is in the mobile phase). Assuming a random process of adsorption, desorption and diffusion in and out of the stagnant fluid, the solute wave velocity becomes

$$u_{solute} = v \left[\frac{\text{amount solute in mobile phase}}{\text{total amount solute in column}} \right] \tag{4}$$

or, after rearrangement

$$u_{solute}(T) = \frac{v}{1 + [(1-\alpha)/\alpha]\epsilon K_d + [(1-\alpha)/\alpha]\,(1-\epsilon)\rho_s(\Delta q/\Delta c)\,K_d} \tag{5}$$

Eq. (5) represents a crude, first order description of movement of solute in the column. With a few additional assumptions this equation can be used to predict the separation in the system.

The most important assumption, and the assumption least likely to be valid, is that the solid and fluid are locally in equilibrium. Then Δq will be related to Δc by the equilibrium adsorption isotherm. This assumption allows us to ignore mass transfer effects. The second assumption is that dispersion and diffusion are negligible; thus, all of the solute will travel at the same average solute velocity. These assumptions greatly oversimplify the physical situation, but they do allow us to make simple predictions. As long as we don't believe these predictions must be exactly correct, the simple model which results can be extremely helpful in understanding separation techniques.

For undergraduate students we limit the theory to simple linear equilibrium of the form

$$q = A(T)c \tag{6}$$

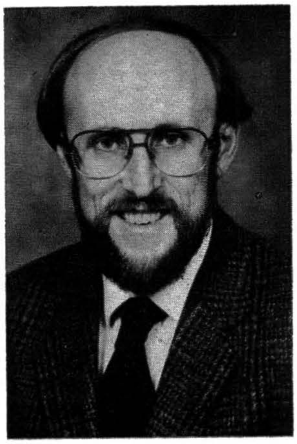
where q is the adsorbed solute concentration, A(T) is the equilibrium constant which is a function of temperature, and c is the solute concentration in the fluid.

For common adsorbents the amount of material adsorbed decreases as temperature is increased. Thus A(T) is a monotonically decreasing function of temperature. With linear equilibrium $\Delta q/\Delta c = A(T)$, and Eq. (5) becomes

$$u_{solute}(T) = \frac{v}{1 + [(1-\alpha)/\alpha]\epsilon K_d + [1-\alpha)/\alpha]\,K_d(1-\epsilon)\rho_s A(T)} \tag{7}$$

For Eq. (7) the solute wave velocity is the same as the average solute velocity. Eq. (7) allows us to explore the behavior of solute in the column for a variety of operating methods.

Several facts about the movement of solute can be deduced from Eq. (5) or Eq. (7). The highest possible solute velocity is v, the interstitial fluid velocity. This will occur when the molecules are very large and $K_d = 0.0$. For small molecules $K_d = 1.0$, and with porous packings these molecules always move slower than the interstitial velocity even when they are not adsorbed. If adsorption is very strong the solute will move very slowly. When the adsorption equilibrium is linear, Eq. (7) shows that the solute velocity does not depend on the solute concentration. This is important and greatly simplifies the analysis for linear equilibria. If the equilibrium is nonlinear, $\Delta q/\Delta c$ will depend on the fluid concentration and Eq. (5) shows that the solute velocity will depend on concentration.



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Nonlinear equilibrium will be considered later.

A convenient graphical representation of the solute movement is obtained on a plot of axial distance, z, versus time. Since the average solute molecule moves at a velocity of $u_{solute}(T)$, this movement is shown as a line with a slope u_{solute}. This is illustrated for a simple chromatographic separation in Fig. 2. Fig. 2A shows the feed pulse while Fig. 2B shows the solute movement in the column. The product concentrations predicted are shown in Fig. 2C. Note that this simple model does not predict dispersion or zone speading, but does predict when the peaks exit.

If desired, zone spreading can be included, but will conceptually complicate the model. The advantage of this model is that it is simple and can be used to understand a variety of methods of operation.

EFFECTS OF CHANGING THERMODYNAMIC VARIABLES

Changes in temperature, pH, ionic strength or solvent concentration are often used to help desorb and elute the solute. Changes in these variables will change the equilibrium constant, A, in Eqs. (6) and (7). With temperature one can either use a jacketed bed and change the temperature of the entire bed (called the direct mode) or he can change the temperature of the inlet stream and have a temperature wave propagate through the column (called the travelling wave mode). For most of the other elution methods the travelling wave mode is used. Elution may be done either cocurrently or countercurrently.

The wave velocities for chemicals added to the system can be obtained from Eq. (5) or (7). The velocity at which temperature moves in the column (the thermal wave velocity) can be obtained from an energy balance. If we can ignore the heat of adsorption and heat of mixing and assume the column is adiabatic, then the energy in the mobile fluid compared to the total energy in mobile fluid, stationary fluid, solid and the column wall in a segment of the column is

$$\frac{\text{Energy in mobile phase}}{\text{Total energy in column segment}} = \frac{(\Delta z A_c)\,\alpha\rho_f C_f\,(T_f - T_{ref})}{[(\Delta z A_c)\,(\alpha + (1-\alpha)\epsilon)\,\rho_f C_f (T_f - T_{ref}) + (\Delta z A_c)\,(1-\alpha)\,(1-\epsilon)\,C_s\rho_s (T_s - T_{ref}) + (\Delta z W)\,C_w\,(T_w - T_{ref})]} \qquad (8)$$

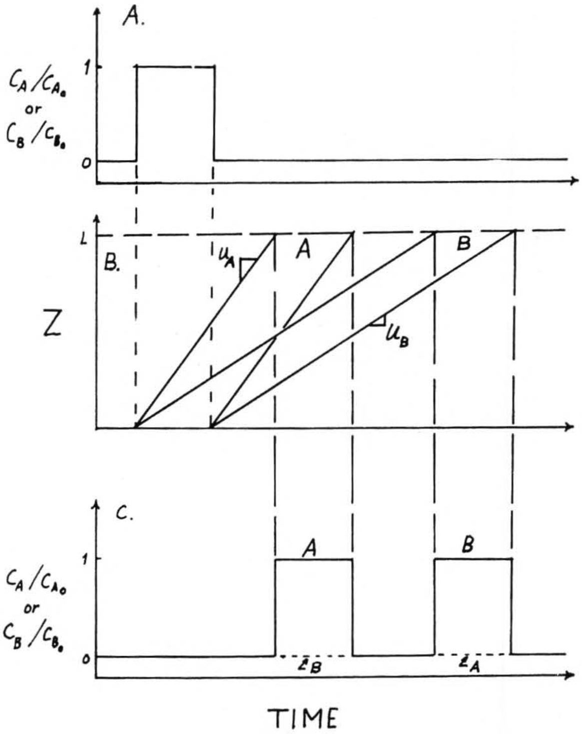

FIGURE 2. Solute movement model for isothermal chromatography: A) Feed pulse; B) Trace of solute movement in column; C) Product concentrations.

In Eq. (8) W is the weight of column wall per length and T_{ref} is any convenient reference temperature. The wall term is only important in laboratory scale columns. The velocity of the thermal wave in the column is just the ratio in Eq. (8) multiplied times the fluid velocity. After assuming local equilibrium so that $T_s = T_f = T_w$ and simplifying, we have

$$u_{thermal} = \frac{v}{1 + [(1-\alpha)/\alpha]\epsilon + [1-\alpha)\,(1-\epsilon)\,C_s\rho_s + (W/A_c)\,C_w]/\alpha\rho\,C_f} \qquad (9)$$

Note that with the simplifying assumptions made here $u_{thermal}$ is independent of temperature. Comparison of Eqs. (9) and (7) show they have a similar form but there is an additional term in Eq. (8) to account for thermal storage in the column wall, and effectively $K_d = 1.0$ for energy changes. Just as Eqs. (5) and (7) represented the movement of the average solute molecule, Eq. (9) represents the average rate of movement of the thermal wave. A more exact analysis is needed to include dispersion and heat transfer rate effects.

On a graph of axial distance z versus time t the thermal wave will be a straight line with a slope $u_{thermal}$. Figure 3 illustrates elution using temperature for counter-current desorption. In this case a single solute is adsorbed. The feed flow is continued until just before solute breakthrough occurs. Then counter-current flow of a hot fluid is used to remove solute. Upon reversing the flow the fluid first exits at the feed temperature and the feed concentration. When the thermal wave breaks through, the temperature and concentration both jump. Since the adsorption equilibrium constant is lower at high temperature the solute velocity can be significantly greater at the higher temperature. In actual practice the outlet temperature and concentration waves will be S-shaped curves because of the dispersion forces.

To complete the analysis of the traveling wave mode we need to consider the change in solute concentration when the adsorbent temperature is changed. The effect of temperature changes on solute concentration can be determined by a mass balance on a differential section of column Δz over which the temperature changes during a time interval Δt. This balance for one solute is

$$\alpha v \Delta t (c_2-c_1) - [\alpha + K_d \epsilon (1-\alpha)](c_2-c_1)\,\Delta z - (1-\alpha)(1-\epsilon) K_d \rho_s (q_2-q_1)\,\Delta z = 0 \qquad (10)$$

where 1 refers to conditions before the temperature shift and 2 to after the shift. In Eq. (10) the first term is the in-out term, the second term is accumulation of solute in the fluid, and the third term is accumulation of solute on the solid. To ensure that all material in the differential section undergoes a temperature change the control volume is selected so that $\Delta t = \Delta z / u_{thermal}$. The mass balance then becomes

$$\left(\alpha + \epsilon(1-\alpha) K_d - \frac{\alpha v}{u_{thermal}}\right)(c_2-c_1) + K_d (1-\alpha)(1-\epsilon)\rho_s (q_2-q_1) = 0 \qquad (11)$$

If we assume that solid and fluid are locally in equilibrium and that the equilibrium isotherm is linear, then Eq. (11) reduces to

$$\frac{c(T_H)}{c(T_c)} = \left(\frac{1}{u_{solute}(T_c)} - \frac{1}{u_{thermal}}\right) \Big/ \left(\frac{1}{u_{solute}(T_H)} - \frac{1}{u_{thermal}}\right) \qquad (12)$$

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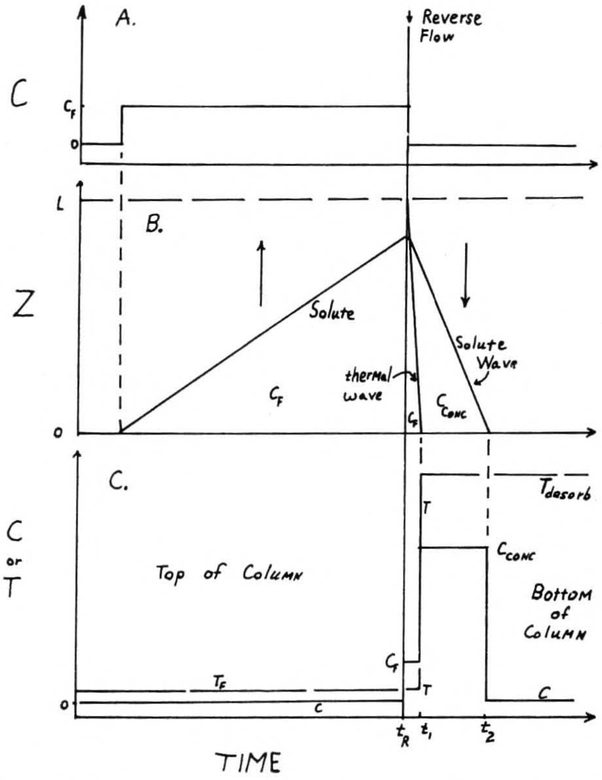

FIGURE 3. Solute movement model for adsorption followed by counter-current elution with a hot fluid: A) Inlet concentration and temperatures; B) Trace of solute and temperature movement in bed; C) Product concentrations and temperatures.

In the typical liquid system $u_{thermal} > u_{solute}(T_H) > u_{solute}(T_c)$, and $C(T_H) > C(T_c)$. Thus the solute is concentrated during elution. This concentration is calculated from Eq. (12), and was plotted on Fig. 3C. Note in Figs. 3A and 3C that the overall mass balance will be satisfied. If the equilibrium constant A does not change very much $u_{sol}(T_H) \approx u_{sol}(T_c)$ and there will be little change in concentration during elution. Since A is not usually strongly dependent on temperature, large temperature changes are required. An alternative is to use

The equations developed here can be rigorously derived from the governing partial differential equations by making a group of assumptions called the local equilibrium assumptions and then using . . . the method of characteristics.

a different eluant which has a major effect on A. Eqs. (11) and (12) are still valid but with u_{Eluant} replacing $u_{thermal}$.

In the direct mode the entire column is heated or cooled simultaneously. In this case $u_{thermal}$ is essentially infinite and Eq. (12) simplifies to

$$\frac{c(T_H)}{c(T_c)} = \frac{u_{solute}(T_H)}{u_{solute}(T_c)} \tag{13}$$

For the usual adsorbent A(T) decreases(solute desorbs) as temperature increases. Thus u_{solute} increases and, as expected, Eq. (13) predicts that the solute concentration increases as temperature increases.

This completes the basic analysis procedure for the solute movement model for linear isotherms. As presented, this is not a rigorous mathematical model but was based on simple physical ideas. The equations developed here can be rigorously derived from the governing partial differential equations by making a group of assumptions called the local equilibrium assumptions and then using a mathematical method called the method of characteristics [1, 22]. Although some of the assumptions required for the rigorous development have been mentioned in passing, it will be helpful to list them explicitly here.

1. Homogeneous packing (no channeling).
2. Radial gradients are negligible.
3. Neglect thermal and pressure diffusion.
4. No chemical reactions except for sorption.
5. Neglect kinetic and potential energy terms.
6. No radiant heat transfer.
7. No electrical or magnetic fields.
8. No changes of phase except sorption.
9. Parameters are constant except for A.
10. Constant fluid velocity.
11a. Column is adiabatic, or
11b. Column is at controlled constant temperature.
12. Heat of adsorption is negligible.
13. Solutes do not interact.
14. Thermal and mass dispersion and diffusion are negligible.
15. Heat and mass transfer rates are very high so that fluid and solid are locally in equilibrium.
16. Equilibrium is linear.

This is a formidable list of assumptions. If any of these assumptions are invalid the predictions can be way off. The most critical assumptions are the last three. Assumptions 14 and 15 cause the outlet concentrations and temperatures to show sharp jumps instead of the experimentally observed S-shaped curves. Alternate mathematical models which are more realistic but much more complex are reviewed by Sherwood *et al* [19]. Assumption 16 can also cause physically impossible predictions, but fortunately this assumption of linear equilibrium is easily relaxed (see the next section).

As we have seen this model greatly oversimplifies the actual fluid flow and heat and mass transfer processes occurring in the column. Because of this the predicted separation is always better than that obtained in practice. What is this model good for? The model is simple and can thus be used to analyze rather complex precesses. The model does predict when the peak maximum will exit and thus is a good guide for setting operating variables. Since this model predicts the best possible separation, the model can be used to determine if, at its best, a separation scheme is of interest. Since the predictions made are qualitatively correct, as long as the model predictions are interpreted in a qualitative or at best semiquantitative sense the model is very useful.

NONLINEAR SYSTEMS

If the equilibrium isotherm is nonlinear the basic structure developed here is still applicable, but we must use Eqs. (5) and (11) instead of (7) and (12). The solute velocity now depends on both temperature and concentration. Once a specific isotherm is determined it can be substituted into Eq. (5). For example, if the Freundlich isotherm

$$q = A(T)c^k \quad k < 1 \tag{14}$$

is used, then

$$\lim_{\Delta c \to 0} \frac{\Delta q}{\Delta c} = \left.\frac{\partial q}{\partial c}\right|_T = k\,A(T)\,c^{k-1} \tag{15}$$

and

$$u_{solute} = \frac{v}{1 + [(1-\alpha)/\alpha]\,\epsilon K_d + [(1-\alpha)/\alpha]\,K_d(1-\epsilon)\,\rho_s k A(T)\,c^{k-1}} \tag{16}$$

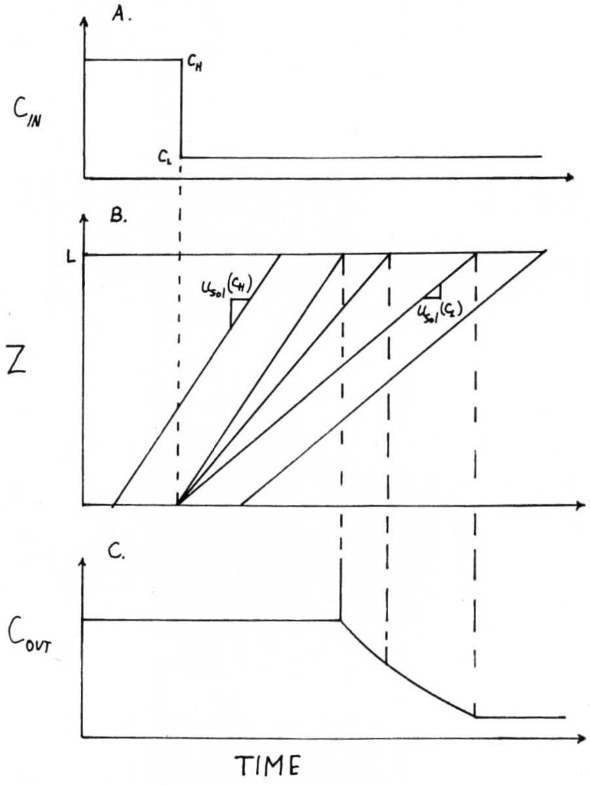

FIGURE 4. Diffuse waves: A) Inlet concentration; B) Solute movement; C) Outlet concentration.

A diffuse wave occurs when a concentrated solution is displaced by a dilute system. This is illustrated in Fig. 4 where the outlet wave concentrations are calculated. If we try the reverse (dilute solution displaced by a concentrated solution) then the limit does not exist since Δc has a finite value. A shock wave occurs. Another way of looking at this is Eq. (16) predicts a lower slope for dilute systems. When a concentrated solution displaces a dilute solution (Fig. 5A), the theory predicts that the solute lines overlap and two different concentrations occur simultaneously (Fig. 5B). This is physically impossible. To avoid this problem a mass balance is done on a finite section of the column of length Δz. This balance is the same as Eq. (10) except 1 refers to before the shock and 2 after the shock. Now we select the time interval $\Delta t = \Delta z / u_{shock}$ so that the shock has passed through the entire section. Solving for the shock wave velocity, we obtain

$$u_{shock} = \frac{v}{1 + [(1-\alpha)/\alpha]\epsilon K_d + [(1-\alpha)/\alpha]\,(1-\epsilon)\;K_d\rho_s\,[(q_2-q_1)/(c_2-c_1)]} \quad (17)$$

This is shown in Fig. 5C and the outlet concentration is calculated in Fig. 5D.

Nonlinear isotherms can result in interesting interactions when various shock and diffuse waves intersect. The mathematical principles involved in switching from differential to finite elements is also a good pedalogical tool for teaching graduate students. For graduate students I rigorously derive all these results using the local equilibrium model and the method of characteristics [19, 22].

COUNTER-CURRENT OPERATION I. Continuous Flow

In most chemical engineering unit operations continuous counter-current flow is used since it is usually the most efficient way to operate. Counter-current movement of solids and fluid is difficult

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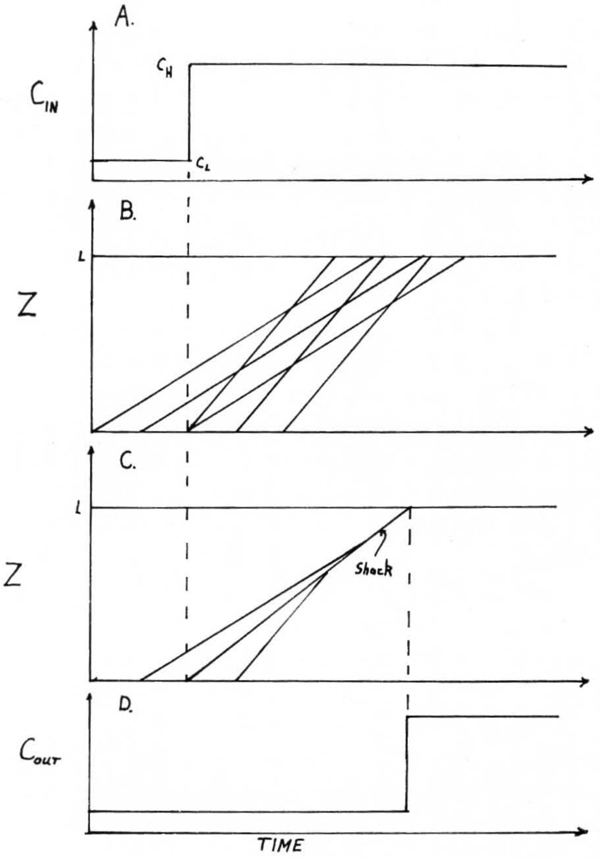

FIGURE 5. Shock wave: A) Inlet concentration; B) Solute waves following Eq. 18; C) Shock wave; D) Outlet concentration.

NEW ADSORPTION METHODS

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to achieve, but has been extensively studied. Counter-current schemes have included flow in open columns [2, 10, 17]; the hypersorption process where solids flow was controlled by the opening and closing of holes in sieve trays [11], moving belt schemes [12] and the recent magnetically stabilized moving bed system developed by Exxon. The idealized analysis of all these systems will be similar.

A counter-current system is shown in Fig. 6. The solids flow down the column while the fluid flows up. The less strongly adsorbed solute A moves up in zone 1 while strongly adsorbed solute B moves down in this zone. Thus zone 1 purifies solute A. Zone 2 removes solute A from B and thus purifies solute B. In zone 3 solute B is desorbed with desorbent D. Zone 4 serves to remove solute A from the desorbent so that desorbent can be recycled. The desorbent could be water or a solvent.

The solute movement theory can be applied to this system. The solute wave velocities calculated from Eq. (5) or (7) were with respect to a stationary solid. The appropriate fluid velocity is then the interstitial fluid velocity relative to the solid. Thus

$$v = \frac{V_{super}}{\alpha} + V_{solid} \qquad (18)$$

where V_{super} is the superficial fluid velocity and V_{solid} is the superficial solid velocity. Now u_{solute} calculated from Eq. (5) or (7) is the solute velocity with respect to the solid. The solute velocity which an observer will see is obtained by subtracting the solids velocity

$$u_{solute\ CC} = u_{solute} - V_{solid} \qquad (19)$$

$u_{solute\ CC}$ is positive when the solute flow is up the column and negative when it flows down.

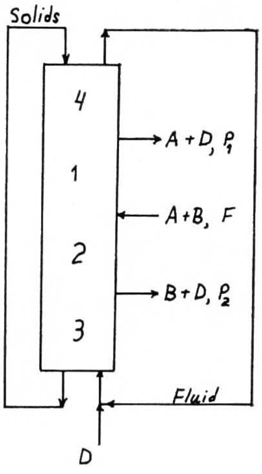

FIGURE 6. Counter-current separator.

In the counter-current column the solids velocity is the same in all zones but the superficial fluid velocity varies from zone to zone since feed is added and products are withdrawn. If we set $V_{super,3}$ as velocity in zone 3, then for relatively dilute systems

$$\begin{aligned} V_{super,2} &= V_{super,3} - P_2/A_C \\ V_{super,1} &= V_{super,2} + F/A_C \qquad (20) \\ V_{super,4} &= V_{super,1} - P_1/A_C \end{aligned}$$

Since V_{super} changes, $u_{solute\ CC}$ will change from zone to zone. In addition, if the desorbent affects the adsorption of solute then the equilibrium constant A(T) will vary from zone to zone and $U_{solute\ CC}$ will change. This latter effect is not necessary to make the counter-current column work.

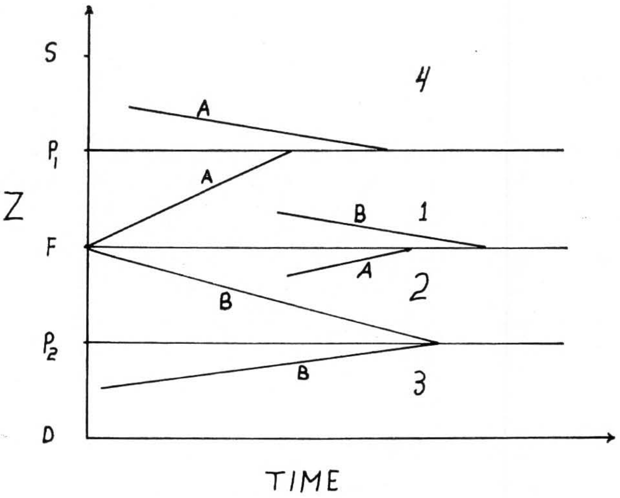

FIGURE 7. Solute movement in continuous counter-current column.

To achieve the separation indicated in Fig. 6 we want solute A to move upward in zones 1 and 2 and downward in zone 4. Thus

$$u_{A\ CC,1} > u_{A\ CC,2} > 0 > u_{A\ CC,4} \qquad (21)$$

Solute B should move downwards in zones 1 and 2 and upwards in zone 3. Thus

$$u_{B\ CC,3} > 0 > u_{B\ CC,1} > u_{B\ CC,2} \qquad (22)$$

An alternative to continuously moving solid down the column is to move solid and entrained fluid down in pulses. This is commonly used in continuous ion exchange systems such as variants of the Higgins system and the Graver Water Treatment System. This system could also be applied to the binary separator.

Eqs. (21) and (22) are an important result since they control the operation of the continuous counter-current column. There is a range of values for P_1, P_2 and D for a given feed flow rate which will satisfy inequalities (21) and (22). In actual practice it is desirable to choose the flow rates so that all the inequalities are as large as possible.

The appropriate solute waves are shown in Fig. 7. In the ideal case at steady state there will be no solute A in zones 4, 2 or 3 and no solute B in zones 1, 3 and 4. Because of dispersion and finite mass transfer rates solute A will appear in zones 4 and 2, and B will be in zones 1 and 3. The size of the zones required depends on these dispersion and mass transfer rate effects. In addition, any axial solid or fluid mixing caused by non-perfect flow will require a larger column. Extreme mixing or channeling can destroy the desired separation.

COUNTER-CURRENT OPERATION II. Pulsed Flow

An alternative to continuously moving solid down the column is to move solid and entrained fluid down in pulses. This is commonly used in continuous ion exchange systems such as variants of the Higgins system [10, 18, 20] and the Graver Water Treatment System [14]. This system could also be applied to the binary separator shown in Fig. 6.

In the pulsed system the solid is stationary except for short periods when it moves down. Thus u_{solute} is given directly by Eq. (5) or (7) with the superficial fluid velocities given by Eq. (20). When the solid and fluid are pulsed downward, the solute waves are also shifted down. The solute wave theory for the pulsed flow system is shown in Fig. 8. The net movement of solute A is upward in zones 1 and 2 and downward in zone 4. The net movement of solute B is downward in zones 1 and 2 and up in zone 3. Fig. 8 is drawn for a plug flow movement of solids and fluids during the downward pulse. Feed would be introduced continuously and withdrawn continuously. Only one feed period was shown to keep the figure simple. If mixing occurs during the pulse less separation will be obtained. This is a practical limit to sharp fractionation of two solutes in a pulsed flow counter-current system.

$$V_{solids,avg} = l_p/t_p \tag{23}$$

where l_p is the length of a pulse movement in meters and t_p is the time between pulses in minutes. The average solute velocity over many pulses is given by Eq. (19). The desired separation will be achieved when inequalities (21) and (22) are satisfied.

SIMULATED COUNTER-CURRENT SYSTEMS

An alternative to moving bed systems is to simulate counter-current movement. This is done with a series of packed bed sections by switching the location of all feed and product withdrawal ports. An observer located at a product withdrawal port sees the solids move downwards everytime the port location is shifted upwards. Thus the observer sees a process very similar to the pulsed counter-current system analyzed in Fig. 8.

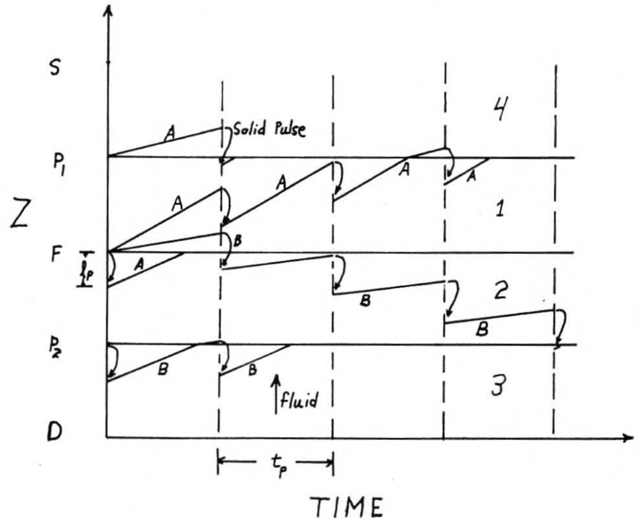

FIGURE 8. Solute movement in pulsed counter-current system.

The first simulated counter-current system was the Shanks system which has been applied to leaching, adsorption and ion exchange [13, 21]. The Shanks system uses a series of columns with plumbing arranged so that feed can be input and

The solute movement theory can be used to analyze the simulated counter-current system in two ways.

product withdrawals removed from any column. Thus the counter-current separator shown in Fig. 6 can be simulated. Modern adaptations of the Shanks process have been done by Barker and his co-workers for gas chromatography systems [3, 5] and for gel permeation chromatography [4]. UOP has extensively used a pilot plant scale system which is a series of columns for scaling up their commercial scale units [9, 16]. The commercial UOP simulated counter-current process, Sorbex, uses a single column with many packed sections and has a rotating valve for distributing feed, desorbent and products. The commercial units simulate the system shown in Fig. 6 [6, 7, 8, 9, 16]. The UOP process was first commercialized as Molex for separation of linear paraffins from branched-chain and cyclic hydrocarbons using 5A molecular sieves. Since then, processes for p-xylene purification (Parex), Olefin separation (Olex), and separation of fructose from glucose (Sarex) have been commercialized. Pilot plant scale separations for a variety of other problems have been demonstrated [9, 16]. A large number of patents have been granted on simulated moving bed systems.

The solute movement theory can be used to analyze the simulated counter-current system in two ways. First, if the observer fixes himself at one of the outlet or inlet ports then he sees the solid and entrained fluid transferred downwards in pulses. This observer then sees solute movement as shown in Fig. 8. The average solids velocity this observer sees is given by Eq. (19), and the analysis applied for the pulsed counter-current operation is applicable.

In the second analysis the observer fixes himself on the ground and he sees the solid as stationary. With the fluid flowing up the column, he sees all the inlet and outlet ports move up the column at discrete times. When a port reaches the top of the column, it recycles back to the bottom. In between the shifting of port locations, the adsorber is a fixed bed system. Thus the solute wave velocity can be determined from Eqs. (5) or (7). The fluid velocities in each section will differ. The superficial fluid velocities are given by Eq. (20) and the interstitial velocity v equals V_{super}/α. The shifting of ports does not shift the solute waves, but does change the wave velocities since it changes which zone the solute is in. This is illustrated in Fig. 9. If the desorbent changes the equilibrium constants this will also change the solute velocities.

Note in Fig. 9 that the movement of both species is up, but the more strongly adsorbed solute B moves down with respect to the port locations. Feed would be introduced continuously at the port marked A + B, but was illustrated for only one time period. The zone numbers corresponding to Fig. 6 are shown on Fig. 9. The fluid velocities and hence the solute velocities are different in each zone. When fluid reaches the top of the cascade it is recycled to the bottom. Thus the solute waves are also recycled. If the timing of the switches is appropriate, solute A will appear in zones 1, 2 and the lower section of zone 4, and solute B will appear in zones 1, 2 and the upper section of zone 3. Solute A goes into zone 4 since only a portion of the fluid is withdrawn as product P_1. Solute B goes into zone 3 because of the switching of ports. Dispersion and mixing effects will naturally spread out the solute waves in each zone.

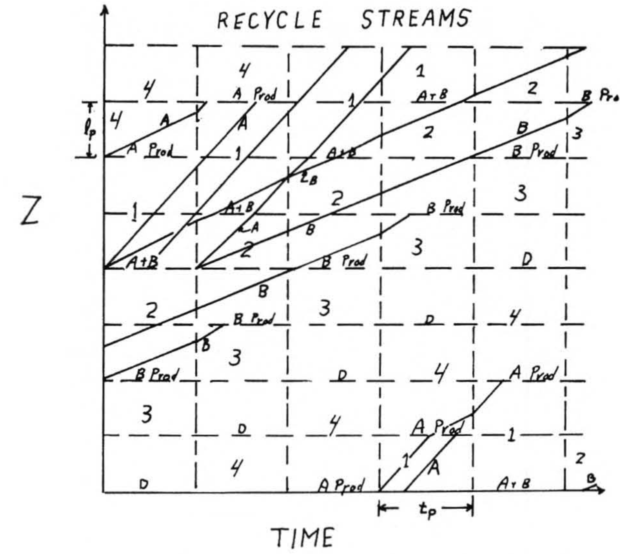

FIGURE 9. Solute movement in simulated counter-current system.

To achieve the desired separation we desire to have solute A move up in zones 1 and 2 faster than the port movement and slower in zone 4. Solute B should move slower than the port movement in zones 1 and 2 and faster in zone 3. The average velocity of port movement is

$$u_{port,avg} = l_{port}/t_{port} \qquad (24)$$

where l_{port} is the packing height between ports and

t_{port} is the time between switches of ports. The conditions to achieve separation are then

$$u_{A,1} > u_{A,2} > u_{port,avg} > u_{A,4} \qquad (25)$$

$$u_{B,3} > u_{port,avg} > u_{B,1} > u_{B,2}$$

These conditions follow the same order as Eqs. (21) and (22).

How close is a simulated counter-current system to a truly counter-current separator? Although the answer to this depends on the chemical system and the column length, Liapis and Rippin [15] found that the simulated system had an adsorbent utilization from 79% to 98% that of the truly counter-current system. With a single zone system they found that from two to four sections were sufficient and that two to four column switches were required to reach a periodic concentration profile.

Comparison of simulated counter-current and truly counter-current systems is of considerable interest. Both systems at steady state can at best do a complete binary separation. Partial separation of additional components can be obtained with side withdrawals. The simulated counter-current system could also be extended to more complex cycles where part of the bed is temporarily operated as a batch chromatograph. The simulated moving bed system is actually a fixed bed system. Thus flooding (unintentional upwards entrainment of solid) will not be a problem, but excessive pressure drop may result for small particles or viscous solutions. The fixed bed will have a lower α and hence a higher capacity than truly counter-current systems, but this will be offset by the distribution zones between sections. The actual movement of solids requires means for keeping the bed stable, may result in excessive attrition, but allows for easy solids replacement or external reactivation. Both systems have mechanical difficulties to overcome. In the simulated moving bed these difficulties are the valving and timing while in an actual moving bed they involve moving the solids without mixing. Currently, the simulated counter-current systems have been the preferred choice for large-scale adsorption installations. □

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NOMENCLATURE

$A(T)$ —Equilibrium parameter, Eq. (6)
A_c —Cross sectional area of column
c —Solute concentration in fluid, kg/L
C_f —Heat capacity of fluid
C_S —Heat capacity of solid
C_w —Heat capacity of wall
F —Feed rate, L/min
k —Exponent in Freundlich isotherm, Eq. (14)
K_d —Fraction of interparticle volume species can penetrate, Eq. (1)
l_p, l_{port} —Length of travel of pulse, or packing height between ports, m
L —Column length, m
P_1, P_2 —Product flow rates, L/min
q —Amount of solute adsorbed, kg/kg adsorbent
t —Time, min
t_p —Time between switching port locations, min
T —Temperature, °C
T_f, T_S, T_w, T_{ref} —Temperature of fluid, solid, wall and reference
T_C, T_H —Cold and hot temperatures
u_A, u_B, u_{solute} —Solute wave velocity, m/min, Eq. (5) or (7)
u_{shock} —Shock wave velocity, m/min, Eq. (17)
$u_{thermal}$ —Thermal wave velocity m/min, Eq. (9)
v —Interstitial fluid velocity, m/min
V_e —Elution volume of non-adsorbed species, L
V_i —Internal void volume, L
V_o —External void volume, L
V_{solid} —Solid velocity, m/min
V_{super} —Superficial fluid velocity, m/min
W —Weight of column wall per length, kg/m
z —Axial distance in column, m
α —Interparticle void fraction
ϵ —Intraparticle void fraction
Δ —Difference calculation
ρ_s —Solid density, kg/L

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BOOK REVIEW: Carnegie-Mellon

Continued from page 37.

Obviously the book is not intended for use in the usual academic sense and its particular audience is the many people . . . faculty, staff and students . . . who have contributed to chemical engineering at Carnegie over the years. It can also serve as a guide to those considering similar undertakings at their own institution in pointing out the monumental effort involved. Admittedly, this reviewer is not wholly unbiased in consideration of this volume inasmuch as he has spent almost half of his academic career at Carnegie, but he can attest to a considerable portion of the accuracy of Professor Rothfus' many details. Its delightful reading!! ☐

ChE books received

"Resource Recovery Economics," Stuart H. Russell; Marcel Dekker Inc., New York 10016; 312 pages, $39.75 (1982)

"Specifying Air Pollution Control Equipment," edited by Richard A. Young, Frank L. Cross, Jr.; Marcel Dekker Inc., New York 10016; 296 pages, $38.50 (1982)

"Introduction to High-Performance Liquid Chromatography," R. J. Hamilton, P. A. Sewell; Chapman & Hall, 733 Third Ave., New York 10017; 183 pages, $29.95 (1982)

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"Heat Transfer in Nuclear Reactor Safety," S. George Bankoff, N. H. Afgan; Hemisphere Publishing Corp., New York 10036; 964 pages, $95.00 (1982)

"Essentials of Nuclear Chemistry," H. J. Arnikar; John Wiley & Sons, Somerset, NJ 08873; 335 pages, $17.95 (1982)

"Technology Transfer and Innovation," Louis N. Mogavero, Robert S. Shane; Marcel Dekker Inc., New York, 10016; 168 pages, $22.50 (1982)

"Solar Heating and Cooling: Active and Passive Design," Second Edition, J. F. Kreider, F. Kreith; Hemisphere Publishing Corp., Washington DC 20005; 479 pages, $29.95 (1982)

"Liquids and Liquid Mixtures," Third Edition, J.S. Rowlinson, F. L. Swinton; Butterworths, Woburn, MA 01801; 328 pages, $69.95 (1982)

"Handbook of Multiphase Systems," edited by G. Hetsroni; Hemisphere Publishing Corp., Washington, DC 20005; $64.50 (1982)

"Liquid Filtration," Nicholas P. Cheremisinoff, David S. Azbel; Butterworth Publishers, Woburn, MA 01801; 520 pages, $49.95 (1983)