An Equilibrium Theory for Sorption Accompanied by Sorbent Bed Shrinking or Swelling

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The swelling and shrinking of ion exchange resins due to ion exchange and/or electrolyte sorption is a commonly observed phenomenon (Helfferich, 1962). However, there have been no attempts to include the effects of this phenomenon in design models for column sorption and ion exchange processes even though 20% changes in resin volume are not unusual (Dow Chemical Company, 1971).

In this paper a design model for the special case of ideally sharp fronts is developed. Additionally the results are used to describe, at least in a qualitative manner, constant pattern front situations.

As a resin particle changes volume it also changes mass. The change in mass of a bed of resin causes a difference between the mass flow rate at the inlet and outlet of the bed. The amount of solute in the bed depends on the inlet and outlet mass flow rates and hence is coupled to the swelling and shrinking phenomenon. If the mass of the resin bed decreases during a saturation operation, then the mass flow rate at the inlet of the bed will be less than the mass flow rate at the outlet of the bed. If the operation is at constant effluent flow rate and one uses a constant density, constant mass flow rate approach based on the effluent flow rate to describe the operation, then the predicted amount of solute in the bed at any time will be greater than the actual amount. Furthermore, the predicted breakthrough time will be less than the actual breakthrough time.

In order to quantitatively determine the effect of the swelling and shrinking phenomenon one must simultaneously solve a solute mass balance and an overall mass balance on the resin bed. This is most easily done by assuming that equilibrium exists and that the front is ideally sharp. Under these assumptions a homogeneous region between the inlet of the bed and the concentration discontinuity (ideally sharp front) contains all the resin that has changed composition, volume, and mass. Therefore, an overall mass balance on the resin bed yields

$$\int_0^t \underset{\text{mass in}}{\text{rate of}}\, dt - \int_0^t \underset{\text{mass out}}{\text{rate of}}\, dt$$

$$= V_N[\epsilon\rho_N + (1-\epsilon)\rho_{rN}] - V_0[\epsilon\rho_0 + (1-\epsilon)\rho_{r0}] \quad (1)$$

where V_N is the volume of the region described above and V_0 is the volume that region would occupy if the resin were in its initial state (see Figure 1). V_N and V_0 are related by the equation $V_N = V_0(D_N/D_0)^3$ where D_N is the diameter of a resin particle in equilibrium with the feed solution and D_0 is the initial particle diameter. The length of the homogeneous region described above is ΔZ so that $V_N = S\Delta Z$ and $V_0 = (D_0/D_N)^3 S\Delta Z$. Using these relations, the overall mass balance becomes

$$\int_0^t \underset{\text{mass in}}{\text{rate of}}\, dt - \int_0^t \underset{\text{mass out}}{\text{rate of}}\, dt$$

$$= S\Delta Z \left\{ \epsilon\rho_N + (1-\epsilon)\rho_{rN} - \left(\frac{D_0}{D_N}\right)^3 [\epsilon\rho_0 + (1-\epsilon)\rho_{r0}] \right\} \quad (2)$$

If one further assumes that the feed solution concentration is constant and that the bed is initially uniform with respect to concentrations, then a solute balance yields

$$x_{AN} \int_0^t \underset{\text{mass in}}{\text{rate of}}\, dt - x_{A0} \int_0^t \underset{\text{mass out}}{\text{rate of}}\, dt$$

$$= S\Delta Z\,[\epsilon\rho_N x_{AN} + (1-\epsilon)\rho_{rN} y_{AN}] - S\Delta Z \left(\frac{D_0}{D_N}\right)^3 [\epsilon\rho_0 x_{A0} + (1-\epsilon)\rho_{r0} y_{A0}] \quad (3)$$

Once the inlet or outlet flow rate is specified the unknown flow rate is eliminated by combining Equations (2) and (3). If one assumes a constant effluent flow rate Q_e, then

$$\Delta Z = \frac{Q_e\rho_0 t/S}{\left(\frac{D_0}{D_N}\right)^3 \left[(1-\epsilon)\rho_{r0}\left(\frac{x_{AN} - y_{A0}}{x_{AN} - x_{A0}}\right) + \epsilon\rho_0 \right] - (1-\epsilon)\rho_{rN}\left(\frac{x_{AN} - y_{AN}}{x_{AN} - x_{A0}}\right)} \quad (4)$$

Similarly if one assumes a constant influent flow rate Q_i, then

$$\Delta Z = \frac{Q_i\rho_N t/S}{\epsilon\rho_N + (1-\epsilon)\rho_{rN}\left(\frac{y_{AN} - x_{A0}}{x_{AN} - x_{A0}}\right) - \left(\frac{D_0}{D_N}\right)^3 (1-\epsilon)\rho_{r0}\left(\frac{y_{A0} - x_{A0}}{x_{AN} - x_{A0}}\right)} \quad (5)$$

If the initial bed length is Z^0 then the final bed length is $(D_N/D_0)^3 Z^0$. At breakthrough, $t = T$, ΔZ is equal to the final bed length so that

$$\Delta Z|_{t=T} = \left(\frac{D_N}{D_0}\right)^3 Z^0 \quad (6)$$

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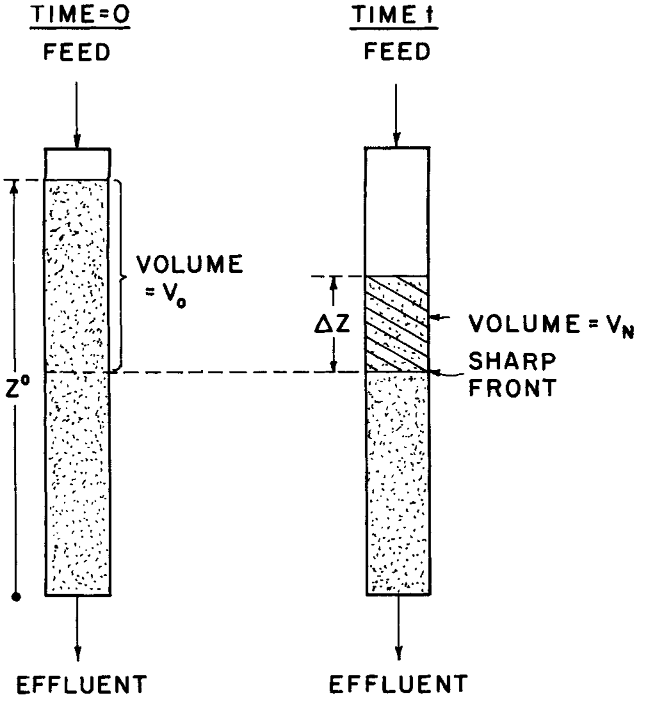

Fig. 1. Geometry of a sharp-front downflow sorption operation accompanied by resin shrinkage.

From this, the expression for the breakthrough time for the constant effluent flow rate case is

$$T = \frac{SZ^0}{Q_e \rho_0} \left\{ \left[(1-\epsilon)\rho_{r0} \left(\frac{x_{AN} - y_{A0}}{x_{AN} - x_{A0}} \right) + \epsilon \rho_0 \right] - \left(\frac{D_N}{D_0} \right)^3 (1-\epsilon)\rho_{rN} \left(\frac{x_{AN} - y_{AN}}{x_{AN} - x_{A0}} \right) \right\} \quad (7)$$

and for the constant influent flow rate case is

$$T = \frac{SZ^0}{Q_i \rho_N} \left\{ \left[\epsilon \rho_N + (1-\epsilon)\rho_{rN} \left(\frac{y_{AN} - x_{A0}}{x_{AN} - x_{A0}} \right) \right] \left(\frac{D_N}{D_0} \right)^3 - (1-\epsilon)\rho_{r0} \left(\frac{y_{A0} - x_{A0}}{x_{AN} - x_{A0}} \right) \right\} \quad (8)$$

The case of the saturation of an initially solute free bed at constant effluent flow rate was discussed briefly above. It was qualitatively argued that the shrinking and swelling phenomenon would have some effect on this process. This can be further illustrated using the above results and a simple numerical example.

The breakthrough time for this problem is described by Equation (7), which can be simplified for this case to

$$T = \frac{SZ^0}{Q_e \rho_0} \left\{ [(1-\epsilon)\rho_{r0} + \epsilon \rho_0] - \left(\frac{D_N}{D_0} \right)^3 (1-\epsilon)\rho_{rN} \left(\frac{x_{AN} - y_{AN}}{x_{AN}} \right) \right\} \quad (9)$$

since $x_{A0} = 0$.

If one uses standard equilibrium theories for static bed sorption to describe this case then the following expression for the breakthrough time would be applied:

$$T = \frac{Z^0 S}{Q} \left[\epsilon + (1-\epsilon) \frac{q_A}{c_A} \right] \quad (10)$$

Since mass flow rate and density are assumed to be constant, $Q = Q_e$. c_A is equal to $x_{AN}\rho_N$ and it is assumed that the equilibrium concentration of solute in the resin is expressed as grams solute sorbed/cc resin fully swollen in pure solvent. Typical equilibrium and swelling data are given by Shurts and White (1957) for the Dowex 50W cation exchange resin (Na^+ form), water, and sodium chloride system. For a feed solution concentration of 20% NaCl the concentrations and physical properties needed to calculate breakthrough times using the expressions above are $x_{AN} = 0.2$, $y_{AN} = 0.0241$, $c_A = 0.228$, $q_A = 0.0277$, $\rho_{r0} = 1.291$, $\rho_0 = 0.9971$, $\rho_{rN} = 1.352$, and $\epsilon = 0.35$. For a column 70 cm long and 2.5 cm in diameter and an effluent flow rate of 30 cc/min the breakthrough time calculated using static bed theory is $T = 4.92$ minutes. Including the effect of shrinking and swelling, the breakthrough time is $T = 5.83$ minutes.

The above example indicates that the effect of sorbent bed shrinking and swelling can be significant and that the direct application of a static bed theory of column design can be inadequate. However, there are situations, such as elution at constant effluent flow rate, where the mass flow rate of solute is independent of the shrinking and swelling phenomenon. For such situations the breakthrough time for ideally sharp frontal behavior depends only on the effluent flow rate, the capacity of the resin, and the void volume, even though the resin bed changes volume during the process. The form of the breakthrough time expression is, therefore, identical to the form developed from static bed equilibrium theory, that is $T = (SZ^0/Q)\,[\epsilon + (1-\epsilon)\, q_A/c_A\,]$. However, one must be careful to specify the correct bed length and the correct equilibrium concentration of the resin. For example, for the elution problem at constant effluent flow rate the mass of solute initially in the void volume is $\epsilon SZ^0 c_A$ where Z^0 is the initial bed length. If the equilibrium concentration of the resin is given in grams solute/cc resin fully swollen in pure solvent, then the mass of solute in the resin is $(1-\epsilon)Z^0(D_N/D_0)^3\, Sq_A$ so that $T = (SZ^0/Q_e)[\epsilon + (1-\epsilon)(D_N/D_0)^3\, q_A/c_A]$. Obviously if q_A were expressed in grams solute/cc resin then the breakthrough time expression would be $T = (SZ^0/Q_e)\,[\epsilon + (1-\epsilon)\, q_A/c_A]$.

One should further note that even though the equations derived above are restricted to a very limiting case the results can be applied, at least in a qualitative manner, to any constant pattern front behavior. For such situations the accumulation of solute in the region containing the front is zero. Therefore, the velocity of the front through the bed is identical to the velocity of the concentration discontinuity calculated from the equations derived above. However, it is not yet possible to calculate the exact position of the constant pattern front relative to the position of the ideal discontinuity except to say that the constant pattern front must intersect the discontinuity at some concentration between x_{A0} and x_{AN}.

It is important to note, however, that use of a static bed theory to describe constant pattern behavior will give incorrect results for the same situations as indicated by the limited theory presented above. Furthermore, the magnitude of the errors will be the same provided that the shrinking and swelling phenomenon does not significantly alter the shape of the front.

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NOTATION

c_A = concentration of solute A in fluid phase, g solute/cm^3 fluid
D = diameter of resin particles, cm
q_A = concentration of solute A in resin phase
Q = fluid flow rate at bed inlet (Q_i) or outlet (Q_e), cm^3/min
S = bed cross-sectional area, cm^2
t = time, min
T = breakthrough time of sharp concentration front, min
V = bed volume, cm^3
x_A = concentration of solute A in fluid phase, g solute/g fluid
y_A = concentration of solute A in resin phase, g solute/g resin phase
Z^0 = initial bed length
ΔZ = length of zone between the bed inlet and the concentration discontinuity, cm

Greek Letters

ϵ = bed void fraction, dimensionless
ρ = density of fluid phase, g/cm^3
ρ_r = density of resin phase, g/cm^3

Subscripts

0 = refers to conditions in the sorption zone between the concentration discontinuity and the outlet of the bed
N = refers to conditions in the sorption zone between the inlet of the bed and the concentration discontinuity

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Reduced State Correlations for the Self-Diffusivity of Dense Fluids

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In a recent article in this journal, correlations for reduced friction coefficients were presented in terms of the reduced density $\rho^* = N\sigma^3/V$ and reduced temperature $T^* = kT/\epsilon$, where σ and ϵ are the collision diameter and well depth respectively for the Lennard-Jones (12, 6) potential (Ramanan and Hamrin, 1972). These correlations were subsequently applied to experimental self-diffusivity data for several dense gases. A degree of success led Ramanan and Hamrin to conclude that "all the information necessary is now available to test theoretical equations for viscosity and thermal conductivity and to compare the results with the numerous experimental values available in the literature."

The purpose of this note is to elaborate on the development of these correlations and to discuss some apparent deficiencies in this approach. Since it is shown that the friction coefficient expressions are based on incorrect assumptions and that inaccurate distribution functions have been used in the calculation of these coefficients, the above conclusion seems unwarranted.

THEORY

In the transport theory proposed by Rice and Allnatt (1961), the pair potential is assumed to consist of a rigid core repulsion superimposed on an arbitrary soft interaction, usually the Lennard-Jones (12, 6) model:

$$\phi(r) = \infty \qquad r < \sigma$$

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad r > \sigma \qquad (1)$$

The friction constant, defined by the Stokes-Einstein equation, can then be separated into hard-core and soft contributions

$$\zeta = \zeta^H + \zeta^S = kT/D \qquad (2)$$

Since the hard-core friction coefficient results from rigid sphere collisions, it can be calculated from the Enskog approach (Longuet-Higgins and Pople, 1956)

$$\zeta^H = \frac{8\rho\sigma^2}{3V}(\pi mkT)^{1/2}\, g(\sigma) \qquad (3)$$

where $g(\sigma)$ is the contact radial distribution function or collision probability. The soft friction coefficient arising from weak attractive interactions in the range $r > \sigma$ is estimated from the linear trajectory approximation (Helfand, 1961)

$$\zeta^S = \frac{8\rho\sigma^2}{3V}(\pi mkt)^{1/2}\left[\frac{\epsilon}{kT}\int_0^\infty F(r)\,\{g(r) - 1\}\right] \qquad (4)$$

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