those given by Shrestha (1970) who used a slightly different constitutive equation. (Both yield the same boundary-layer equations for plane flow.) For flat plate flow both the second-order skin-friction coefficient and displacement-thickness integral are seen to be increased by injection and decreased by suction. For axisymmetric stagnation-point flow the behavior is more complicated as indicated by the last set of entries in Table 1.

CONCLUSION

In the present note the method of local similarity was used to obtain approximate solutions for laminar boundary-layer flows of second-order liquids on wedges and cones. Numerical results were presented to illustrate the effect of the value of the vertex angle of the body and the amount of suction or injection present at the body surface on the second-order skin-friction coefficient and displacement thickness integral.

NOTATION

L = characteristic length
n^* = dimensional normal coordinate (body surface is at $n^* = 0$)
n = $R^{1/2} n^*/L$
p = surface-speed index
R = $\rho L U/\eta_0$
s^* = dimensional tangential coordinate (body vertex is at $s^* = 0$)
s = s^*/L
u^* = dimensional tangential velocity
u = u^*/U
U = inviscid surface speed at $s^* = L$
v^* = dimensional normal velocity
v = $R^{1/2} v^*/U$
V_w = injection function
η_0 = viscosity
μ_1 = material constant
μ_2 = material constant
ρ = mass density

LITERATURE CITED

Coleman, B. D., and W. Noll, "An Approximation Theorem for Functionals with Applications in Continuum Mechanics," *Arch. Rat. Mech. Anal.*, **6**, 5 (1960).

Davis, R. T., "Boundary-Layer Theory for Viscoelastic Liquids," *Proc. 10th Midwestern Mechanics Conf.*, 1145 (1967).

Denn, M. M., "Boundary Layer Flows of a Class of Elastic Liquids," *Chem. Eng. Sci.*, **22**, 3 (1967).

Markovitz, H., and B. D. Coleman, "Incompressible Second-Order Fluids," in *Adv. Appl. Mechanics*, **8**, 69, Academic Press, New York (1964).

Peddieson, J., "Boundary-Layer Solutions for Viscoelastic Liquids," *Proc. 12th Midwestern Mechanics Conf.*, 153 (1971).

Richtmyer, R. D., and K. W. Morton, *Difference Methods for Initial Value Problems*, 2nd ed., chapt. 8, Interscience, New York (1967).

Rivlin, R. S., "The Relation Between Flow of Non-Newtonian Fluids and Turbulent Newtonian Fluids," *Quart. Appl. Math.*, **15**, 212 (1957).

Rosenhead, L. (ed.), "Laminar Boundary Layers" pp. 234, 429, Oxford Univ. Press, London (1963).

Shrestha, G. M., "Elasticoviscous Boundary Layer Flows with Suction," *J. Appl. Phys.*, **41**, 3999 (1970).

Van Dyke, M., "Higher Approximations in Boundary-Layer Theory, Part 3. Parabola in Uniform Stream," *J. Fluid Mech.*, **19**, 145 (1964a).

———., *Perturbation Methods in Fluid Mechanics*, pp. 121-147, Academic Press, New York (1964b).

Manuscript received July 31, 1972; revision received November 27, 1972 and accepted December 4, 1972.

Gas-Solid Chromatography with Nonuniform Adsorbent Surfaces

NEIL A. DOUGHARTY

Department of Chemical Engineering
University of California, Davis, California 95616

Chromatography has been used both as an important application of adsorption and as a means for its study. Chromatographic moment-analysis methods have recently been employed (Grubner, 1968; Schneider and Smith, 1968; Padberg and Smith, 1968; Adrian and Smith, 1970) to evaluate parameters for a variety of transport, adsorption, and reaction processes in packed beds. That analytical relations can be derived affords a convenient opportunity to examine some implications of the details of the assumed process models (Dougharty, 1972).

It is well known that most practical adsorbent surfaces exhibit heterogeneity with respect to their interactions with adsorbing gases. It is the purpose of this note to explore briefly the consequences of surface nonuniformity for the response of packed chromatographic beds.

BEDS OF MIXED ADSORBENTS

Consider first the case of adsorption by a bed of homogeneously mixed, individually uniform, porous solid adsorbents. For spherical packing particles, uniformity over the column cross section, and linear adsorption/desorption rates, one has

$$\frac{\partial c_{a,j}}{\partial t} = k_{a,j}\,(c_{i,j} - c_{a,j}/K_{a,j}), \quad j = 1, \ldots, n \qquad (1)$$

$$\epsilon_{p,j}\,\frac{\partial c_{i,j}}{\partial t} = D_{i,j}\left(\frac{\partial^2 c_{i,j}}{\partial r^2} + \frac{2}{r}\,\frac{\partial c_{i,j}}{\partial r}\right) - \rho_{p,j}\,\frac{\partial c_{a,j}}{\partial t}, \quad j = 1, \ldots, n \qquad (2)$$

$$\epsilon_b\,\frac{\partial c_e}{\partial t} = -\,\epsilon_b\, v\,\frac{\partial c_e}{\partial z} + D_A\,\frac{\partial^2 c_e}{\partial z^2} - (1 - \epsilon_b)\sum_{j=1}^{n} \omega_j\,\frac{3}{R_j}\,k^*_{m,j}\,(c_e - c_{i,j}|_{r=R_j}) \qquad (3)$$

The last term gives the locally volume-averaged rate of mass transfer from the interparticle volume to the intraparticle volume, per unit bed volume. ω_j can be expressed readily in terms of the adsorbent weight fractions, porosities, and densities.

For initial and boundary conditions corresponding to the injection of a rectangular pulse of duration t_0,

$$c_{a,j} = 0 \text{ at } t = 0 \text{ for all } z, r, \text{ and } j \tag{4}$$

$$c_{i,j} = 0 \text{ at } t = 0 \text{ for all } z, r, \text{ and } j \tag{5}$$

$$c_{i,j} = \text{finite at } r = 0 \text{ for all } t \text{ and } j \tag{6}$$

$$c_e = 0 \text{ at } t = 0 \text{ for all } z \tag{7}$$

$$c_e = c_0 \text{ at } z = 0 \text{ for } 0 < t \leq t_0 \tag{8}$$

$$c_e = 0 \text{ at } z = 0 \text{ for } t > t_0 \tag{9}$$

$$c_e = \text{finite at } z \to \infty \text{ for all } t, \tag{10}$$

the system of equations is readily solved for the Laplace transform of c_e,

$$\mathcal{L}[c_e(z, t)] = (c_0/s)(1 - e^{-st_0})\, e^{\lambda_m z} \tag{11}$$

Relating this transform (for example, Schneider and Smith, 1968) to the moments of the chromatographic output $c_e(t)$ for a bed of length L yields

$$\mu_1' = \frac{t_0}{2} + (L/v) \left[1 + \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \sum_{j=1}^{n} \omega_j\, (\epsilon_{p,j} + \rho_{p,j}\, K_{a,j}) \right] \tag{12}$$

and

$$\begin{aligned} \mu_2 = {} & \frac{t_0^2}{12} + 2(L/v) \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \sum_{j=1}^{n} \omega_j\, \rho_{p,j}\, K_{a,j}^2/k_{a,j} \\ & + 2(L/v)(D_A/\epsilon_b v^2) \left[1 + \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \sum_{j=1}^{n} \omega_j (\epsilon_{p,j} + \rho_{p,j}\, K_{a,j}) \right]^2 + 2(L/v) \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \\ & \sum_{j=1}^{n} \omega_j\, (\epsilon_{p,j} + \rho_{p,j}\, K_{a,j})^2 \frac{R_j^2}{15\, D_{i,j}} (1 + 5D_{i,j}/k^*_{m,j} R_j) \end{aligned} \tag{13}$$

If, instead of being mixed, the adsorbents are employed as a series of n successive beds, each containing only a single adsorbent, one finds at the discharge from the last bed, for initial and boundary conditions analogous to those given above

$$\mathcal{L}[c_e(L, t)] = \frac{c_0}{s} (1 - e^{-st_0}) \exp \left[\sum_{j=1}^{n} \lambda_j L_j \right] \tag{14}$$

This yields for the moments

$$\mu_1' = \frac{t_0}{2} + \sum_{j=1}^{n} \frac{L_j}{v_j} \left[1 + \frac{1 - \epsilon_{b,j}}{\epsilon_{b,j}} (\epsilon_{p,j} + \rho_{p,j}\, K_{a,j}) \right] \tag{15}$$

$$\begin{aligned} \mu_2 = {} & \frac{t_0^2}{12} + 2 \sum_{j=1}^{n} \frac{L_j}{v_j} \left(\frac{1 - \epsilon_{b,j}}{\epsilon_{b,j}} \right) \\ & \left[\rho_{p,j} \frac{K_{a,j}^2}{k_{a,j}} + \frac{R_j^2}{15\, D_{i,j}} (\epsilon_{p,j} + \rho_{p,j}\, K_{a,j})^2 \right. \\ & \left. \left(1 + \frac{5\, D_{i,j}}{k_{m,j}\, R_j} \right) \right] + 2 \sum_{j=1}^{n} \frac{L_j}{v_j} \left(\frac{D_{A,j}}{\epsilon_{b,j} v_j^2} \right) \\ & \left[1 + \frac{1 - \epsilon_{b,j}}{\epsilon_{b,j}} (\epsilon_{p,j} + \rho_{p,j}\, K_{a,j}) \right]^2 \end{aligned} \tag{16}$$

Upon comparing Equations (15) and (16) with Equations (12) and (13), one sees that if

$$\epsilon_{b,1} = \ldots = \epsilon_{b,j} = \ldots = \epsilon_{b,n} = \epsilon_b,$$

$$D_{A,1} = \ldots = D_{A,j} = \ldots = D_{A,n} = D_A,$$

and

$$k_{m,j} = k^*_{m,j} \text{ for all } j = 1, \ldots, n,$$

one obtains exactly the same results for the moments for a series of beds as for a single, mixed bed containing the individual adsorbents in the same proportions. These restrictions would be expected to be satisfied approximately for adsorbent particles of equal size packed to equal bed void fractions. No advantages thus are to be expected of mixed beds over the performance of beds in series, each bed in the latter case making simply an additive contribution to the moments.

HETEROGENEOUS ADSORBENTS

Next, consider the case in which a given adsorbent particle is macroscopically uniform but the adsorption sites within the vicinity of a point on the surface possess a distribution of equilibrium constants and/or adsorption rate constants. If adsorption and desorption at sites of given k_a and K_a are assumed to be linear processes, one can write

$$\frac{\partial\, c_a(k_a, K_a)}{\partial t} = k_a \left[c_i - \frac{c_a(k_a, K_a)}{K_a} \right] \tag{17}$$

there being in general a double continuum of such equations. An overall linear equilibrium relation results from this model, but the adsorption kinetics generally will not exhibit the simple behavior of adsorption on a uniform surface. The model may be a reasonable representation of many heterogeneous surfaces at low coverages. It is implied here that c_a can change only by direct adsorption and desorption. For c_i and c_e one has for this case

$$\begin{aligned} \epsilon_p \frac{\partial c_i}{\partial t} = {} & D_i \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} \right) \\ & - \rho_p \int_0^\infty \int_0^\infty \frac{\partial c_a(k_a, K_a)}{\partial t} f(k_a, K_a)\, dk_a\, dK_a \end{aligned} \tag{18}$$

and

$$\begin{aligned} \epsilon_b \frac{\partial c_e}{\partial t} = {} & - \epsilon_b\, v \frac{\partial c_e}{\partial z} + D_A \frac{\partial^2 c_e}{\partial z^2} \\ & - (1 - \epsilon_b) \frac{3}{R} k_m (c_e - c_i|_{r=R}) \end{aligned} \tag{19}$$

These are to be solved, subject to the same initial and boundary conditions as given in Equations (4) to (10), with the subscript j deleted from Equations (4) to (6). The solution is

$$\mathcal{L}[c_e(z, t)] = (c_0/s)(1 - e^{-st_0}) e^{\lambda_h z} \tag{20}$$

and the moments are

$$\mu_1' = \frac{t_0}{2} + (L/v) \left[1 + \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) (\epsilon_p + \rho_p <K_a>) \right] \tag{21}$$

and

$$\mu_2 = \frac{{t_0}^2}{12} + 2(L/v)\left(\frac{1-\epsilon_b}{\epsilon_b}\right)\Bigg[\rho_p <{K_a}^2/k_a> + \frac{R^2}{15D_i}(\epsilon_p + \rho_p <K_a>)^2\left(1 + 5\frac{D_i}{k_m R}\right)\Bigg] + 2(L/v)\left(\frac{D_A}{\epsilon_b v^2}\right)\left[1 + \frac{1-\epsilon_b}{\epsilon_b}(\epsilon_p + \rho_p <K_a>)\right]^2 \tag{22}$$

From appropriate experiments and data analysis (for example, Schneider and Smith, 1968), one would be able to determine adsorption parameters in the forms of $<K_a>$ and $<{K_a}^2/k_a> = <K_a/k_d> = <k_a/{k_d}^2>$. The former is identical with the equilibrium constant one would determine from static adsorption experiments. However, the latter involves a weighted average of the k_a and K_a specific to the chromatographic situation and not simply available from any arbitrary transient experiment. Furthermore, one notes that the moment analysis in turn yields values not directly applicable to most other transient situations (except insofar as higher moments, if they could be measured with adequate precision, would yield other means of the adsorption parameters, from which in principle the full distribution might be reconstructed).

Simple kinetic models serve well in a variety of applications. However, linear isotherms and linear moment-analysis plots for ${K_a}^2/k_a$ are not sufficient to establish the adequacy of a uniform-surface linear kinetic expression for adsorption.

One notes, then, that accurate values of the parameters necessary for a priori packed-bed adsorber or chromatograph design may not be available from batch transient data in the case of heterogeneous adsorbents. Conversely, chromatographic kinetic data for adsorption may yield inaccurate predictions for other adsorber designs, for heterogeneous surfaces.

$$\lambda_h = \frac{\epsilon_b v}{2D_A}\left\{1 - \sqrt{1 + \frac{4D_A}{\epsilon_b v^2}\left[s + \left(\frac{1-\epsilon_b}{\epsilon_b}\right)\left(\frac{3}{R}k_m\right)\frac{\alpha R - \tanh \alpha R}{\alpha R + (\mathrm{k}_m R/D_i - 1)\tanh \alpha R}\right]}\right\}$$

$$\lambda_j = \frac{\epsilon_{b,j} v_j}{2D_{A,j}}\left\{1 - \sqrt{1 + \frac{4D_{A,j}}{\epsilon_{b,j} {v_j}^2}\left[s + \left(\frac{1-\epsilon_{b,j}}{\epsilon_{b,j}}\right)\left(\frac{3}{R_j}k_{m,j}\right)\frac{\alpha_j R_j - \tanh \alpha_j R_j}{\alpha_j R_j + (k_{m,j}R_j/D_{i,j} - 1)\tanh \alpha_j R_j}\right]}\right\}$$

$$\lambda_m = \frac{\epsilon_b v}{2D_A}\left\{1 - \sqrt{1 + \frac{4D_A}{\epsilon_b v^2}\left[s + \frac{1-\epsilon_b}{\epsilon_b}\sum_{j=1}^{n}\omega_j\left(\frac{3}{R_j}{k^*}_{m,j}\right)\frac{\alpha_j R_j - \tanh \alpha_j R_j}{\alpha_j R_j + ({k^*}_{m,j}R_j/D_{i,j} - 1)\tanh \alpha_j R_j}\right]}\right\}$$

NOTATION

c_a = concentration of adsorbate adsorbed, mole/g of adsorbent

c_e = concentration of adsorbate in the interparticle volume, mole/cm^3

c_i = concentration of adsorbate in the intraparticle pore volume, mole/cm^3

c_0 = concentration of adsorbate in input pulse, mole/cm^3

$\mathfrak{D}$ = molecular diffusivity of adsorbate in fluid phase, cm^2/s

D_A = effective axial dispersion coefficient, cm^2/s

D_i = effective intraparticle diffusivity, cm^2/s

$f(k_a, K_a)$ = adsorption-parameter distribution function, such that $f(k_a, K_a)\,dk_a\,dK_a$ is the fraction of the surface having adsorption rate coefficients between k_a and $k_a + dk_a$ and equilibrium constants between K_a and $K_a + dK_a$

$$<g(k_a, K_a)> = \int_0^\infty \int_0^\infty g(k_a, K_a)\, f(k_a, K_a)\, dk_a\, dK_a$$

k_a = adsorption rate coefficient, cm^3/s-g

K_a = adsorption equilibrium constant, cm^3/g

k_d = desorption rate coefficient, 1/s

k_m = mass-transfer coefficient for transfer between interparticle fluid and external particle surface, cm/s

${k^*}_{m,j}$ = mass transfer coefficient for the j-th adsorbent in a mixed-adsorbent bed, cm/s

L = bed length, cm

r = radial distance from center of a particle, cm

R = particle radius, cm

s = Laplace transform parameter, 1/s

t = time, s

t_0 = duration of the input-pulse injection, s

v = average interparticle axial velocity, cm/s

z = axial distance from column entrance, cm

$_j$ = property of the jth adsorbent or of the jth bed in series

Greek Letters

$$\alpha = \sqrt{\frac{s}{D_i}\left(\epsilon_p + \rho_p \left<\frac{k_a K_a}{s\,K_a + k_a}\right>\right)}$$

$$\alpha_j = \sqrt{\frac{s}{D_{i,j}}\left(\epsilon_{p,j} + \frac{\rho_{p,j}\,k_{a,j}\,K_{a,j}}{s\,K_{a,j} + k_{a,j}}\right)}$$

ϵ_b = bed void fraction, exclusive of intraparticle voids

ϵ_p = intraparticle void fraction

μ_1' = first absolute moment of chromatographic output response, s

μ_2 = second central moment of chromatographic output response, s^2

ρ_p = particle density, g/cm^3

ω_j = volume fraction of jth adsorbent, exclusive of interparticle voids

LITERATURE CITED

Adrian, J., and J. M. Smith, "Chemisorption Rates by Chromatography—Hydrogen on Cobalt," *J. Catal.*, **18**, 57 (1970).

Dougharty, N. A., "Effect of Adsorbent Particle-Size Distribution in Gas-Solid Chromatography," *AIChE J.*, **18**, 657 (1972).

Grubner, O., "Statistical Moments Theory of Gas-Solid Chromatography: Diffusion-Controlled Kinetics," *Advan. Chromatography*, **6**, 173 (1968).

Padberg, G., and J. M. Smith, "Chemisorption Rates by Chromatography," *J. Catal.*, **12**, 172 (1968).

Schneider, P., and J. M. Smith, "Adsorption Rate Constants from Chromatography," *AIChE J.*, **14**, 762 (1968).

Manuscript received August 10, 1972; revision received October 25, 1972 and accepted December 13, 1972.