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GAS–LIQUID–SOLID CHROMATOGRAPHY: EFFECTS OF ADSORPTION AND PARTITIONING

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SUMMARY

The relative effects of gas–solid adsorption and gas–liquid absorption on chromatography are studied. The system is a packed column of porous particles, whose pore surfaces are partially covered with a thin liquid film. Differential equations for the relevant transport processes are used to generate first and second temporal moment expressions for output peaks. These results reduce to more specialized expressions for moments for gas–liquid partition chromatography or gas–solid adsorption chromatography. Effect of partial coverage on retention time and height equivalent to a theoretical plate is discussed.

INTRODUCTION

In gas–liquid chromatography (GLC), a thin layer of liquid is spread on pore surfaces. As the amount of liquid is decreased, partial coverage of pore surfaces may develop so that contact between the gas and solid occurs. For the resulting gas–liquid–solid chromatography (GLSC), gas–solid adsorption effects will be added to the gas–liquid absorption (partitioning) effects. Since GLSC has several advantages over either GLC or gas–solid chromatography (GSC), its continued study is of considerable interest[1]. A significant problem of designing GLSC systems is predicting the optimum liquid–solid ratio of the packing material. A sound theoretical model is obviously desirable for solving this problem. The model presented in this paper describes the essential mass transfer resistances in GLSC, namely, longitudinal dispersion, mass transfer from the mobile phase to the particle surface and intraparticle (pore) diffusion. The rate of adsorption at the gas–solid interface is also included in the model. The equilibrium and rate processes are linear; this facilitates the analysis that allows the properties of the outlet peaks to be derived. While mathematical models that ignore mass transfer resistances may be solved for non-linear equilibrium relations[2], our belief is that the mass transfer resistances are no less important in many cases, and therefore worthy of serious attention.

In what follows we show how the model of gas–liquid partition chromatography[3] may be modified to include gas–solid adsorption effects. The partial differential equations representing mass balances in the interparticle and intraparticle voids are

solved in the Laplace domain. The temporal moments are calculated from the Laplace transform expression for the gas concentration at the column exit. The normalized first moment is the retention time, which represents the cumulative capacity of the column. Column efficiency in the form of the height equivalent to a theoretical plate (HETP) is related to the second central moment, and the effect of liquid load is discussed.

THEORETICAL

Mathematical model

We consider a column of length L packed with porous spherical particles of radius R. The fraction of voids external to the particles is α, and the porosity of particles is β. The superficial velocity $u_0 = \alpha u$ is the volumetric flow-rate divided by the column cross-sectional area.

The point differential mass balance equation[4] for interparticle concentration $c(t,z)$ in the mobile (gas) phase is:

$$\alpha \frac{\partial c}{\partial t} + u_0 \frac{\partial c}{\partial z} = D_0 \frac{\partial c^2}{\partial z^2} - \frac{3}{R}(1-\alpha) k_f [c - c_i (r = R)] \tag{1}$$

with initial condition:

$$c(t = 0,z) = 0 \tag{2}$$

and boundary conditions:

$$c(t,z = 0) = c_0(t) \tag{3}$$

$$c(t,z \to \infty) = \text{finite} \tag{4}$$

Continuity of flux[4] at the outer particle surface serves as a boundary condition that couples the concentration $c(z,t)$ to the intraparticle concentration $c_i(z,r,t)$:

$$D_i \left(\frac{\partial c_i}{\partial r}\right)_{r=R} = k_f[c - c_i (r = R)] \tag{5}$$

The intraparticle mass balance equation[4] must include absorption into the liquid film as well as adsorption at the exposed solid surface. In terms of the liquid phase concentration $c_l(t)$ and solid phase surface concentration $c_a(t)$, we have:

$$\beta \frac{\partial c_i}{\partial t} = D_i \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r}\right) - V_1 \frac{\partial c_1}{\partial t} - A_s \frac{\partial c_a}{\partial t} \tag{6}$$

with initial conditions:

$$c_i(r,t = 0) = 0 \tag{7}$$

$$c_1(t = 0) = 0 \tag{8}$$

$$c_a(t = 0) = 0 \tag{9}$$

In addition to eqn. 5 we have the boundary condition expressing symmetry at the particle center,

$$\left(\frac{\partial c_i}{\partial r}\right)_{r=0} = 0 \tag{10}$$

Instantaneous equilibrium is assumed to be established between the liquid and the gas phase within the pores,

$$K = c_l/c_i \tag{11}$$

From which we have

$$\partial c_l/\partial t = K \, \partial c_i/\partial t \tag{12}$$

Ignoring diffusion in the liquid film will usually be justified for the extremely thin films of GLSC. When the stationary liquid phase is near the monolayer level, its properties may be quite different from the bulk liquid. Here we assume that eqn. 11 applies to the monolayer with the expectation that the equilibrium coefficient K will have different values for monolayer and bulk phases. Such a continuum approach to equilibrium, as well as transport phenomena in thin films has been successful in other contexts (see *e.g.* ref. 5).

A first-order gas–solid adsorption rate expression[4] is assumed:

$$\partial c_a/\partial t = k_a \, (c_i - c_a/K_a) \tag{13}$$

The coefficients k_a and K_a represent the adsorption rate constant (cm/sec) and adsorption equilibrium constant (cm^3/cm^2), respectively.

The set of differential eqns. 1–13 can be solved in the Laplace domain:

$$\bar{c}\,(s) = \bar{c}_0\,(s)\,\exp{(\lambda Z)} \tag{14}$$

where λ is given by:

$$\lambda = \frac{u_0}{2D_0} - \left\{\left(\frac{u_0}{2D_0}\right)^2 + \frac{\alpha}{D_0}\left[s + \frac{3(1-\alpha)\,k_f}{\alpha R}\,(1 - P(s))\right]\right\}^{\frac{1}{2}} \tag{15}$$

with

$$P(s) = \frac{\sin h\,(bR)}{\dfrac{D_i\,b}{k_f}\cos h\,(bR) + \left(1 - \dfrac{D_i}{Rk_f}\right)\sin h\,(bR)} \tag{16}$$

$$bR = \left\{\frac{\beta R^2}{D_i}\,s\left[1 + \frac{V_1\,K}{\beta} + \frac{A_s}{\beta}\,\frac{k_a}{\left(s + \dfrac{k_a}{K_A}\right)}\right]\right\}^{\frac{1}{2}} \tag{17}$$

Moment expressions

Following the usual procedure[4] of using the Laplace transform as a generating function for moments, we obtain the following expressions for the first reduced moment, and second central moment:

$$\mu_1 (z) = \mu_1 (z = 0) + \frac{z}{u} (1 + \delta_0) \tag{18}$$

where:

$$\delta_0 = \frac{(1 - \alpha)\beta}{\alpha} \left(1 + \frac{V_1 K}{\beta} + \frac{A_s K_A}{\beta} \right) \tag{19}$$

and

$$\mu_2' (z) = \mu_2' (z = 0) + \frac{2z}{u} \left[\frac{D_0}{u^2} (1 + \delta_0)^2 + \delta_1 + \delta_2 \right] \tag{20}$$

where:

$$\delta_1 = \frac{1}{15} \left(\frac{1}{D_i} + \frac{5}{Rk_f} \right) \left(\frac{1 - \alpha}{\alpha} \right) \beta^2 R^2 \left(1 + \frac{V_1 K}{\beta} + \frac{A_s K_A}{\beta} \right)^2 \tag{21}$$

$$\delta_2 = \frac{(1 - \alpha)}{\alpha} \frac{K_a^2 A_s}{k_a} \tag{22}$$

In the absence of adsorption, $K_a = 0$, and the moment expressions obtained in this section reduce to those for a model that ignores liquid phase diffusion[3]. In the absence of the liquid phase, we have $V_1 = 0$, and the moment expressions reduce to those of the adsorption model of Suzuki and Smith[4].

The change in first moment, $\mu_1 (z) - \mu_1 (z = 0)$, is the mean retention time t_R for the solute. For GLC, the retention time is:

$$t_R = \frac{z}{u} \left[1 + \frac{(1 - \alpha)\beta}{\alpha} \left(1 + \frac{V_1 K}{\beta} \right) \right] \tag{23}$$

while for GLSC combining eqns. 18 and 19 indicates:

$$t_R = \frac{z}{u} \left[1 + \frac{(1 - \alpha)\beta}{\alpha} \left(1 + \frac{V_1 K}{\beta} + \frac{A_s K_A}{\beta} \right) \right] \tag{24}$$

That is, the overall retention time is the summation of the individual retention times of the different capacities in the column. The mean region retention time is equal to the holdup in the region divided by the flow-rate through the system as a whole. For example, the retention time for the intraparticle gas phase is gas holdup in the pores divided by the throughput flow-rate:

$$t_g = \frac{z}{u} \frac{(1 - \alpha)\beta}{\alpha} \tag{25}$$

An important result for this system, which has no mass sources or irreversible sinks, is that the overall retention time (first moment) depends only on geometrical and equilibrium properties of the column and the packing and not on mass transfer properties. The first moment, therefore, does not depend on how fast equilibrium is developed in the column, and in fact can easily be established by a mass balance.

Effect of liquid load on retention time

Since retention time in a chromatographic column is the summation of the retention times of the different regions in the column, we may write:

$$t_R = t_m + t_g + t_l + t_a \tag{26}$$

where t_m = retention time of the mobile phase, t_g = intraparticle gas retention time, t_l = liquid phase retention time and t_a = retention time caused by adsorption.

The first effect of submonolayer concentration of a non-volatile liquid on a homogeneous adsorption medium is to decrease the retention time of eluates, because of the reduction of the specific area available to the gaseous adsorbate, *i.e.*, t_a decreases. Under the same conditions if the adsorbing medium is more porous, the rate of decrease of retention time is higher since high surface area is associated with the porous medium[1]. Moreover, the reduction of the solid surface involves the decrease of adsorption configurational entropy owing to a decrease in the number of possible ways of arranging molecules among the surface sites[1]. Hence there is an additional contribution to the decrease of retention of eluate which is significant when the first layer of macromolecules nears completion. Examples of decrease of retention time with increasing liquid/solid ratio are shown in refs. 6 and 7. As soon as a monolayer is formed, no further decrease of the mean retention is observed[1]. On the contrary, a slight but steady increase takes place as the percentage of the liquid is increased, *i.e.*, t_l dominates as δ increases steadily. If the liquid does not cover the solid surface evenly as a monolayer, but instead fills the pores before all the solid is covered, then the minimum obtained in the retention time *vs.* liquid load plot will be reached at a higher value of t_R, because of the gas–liquid partitioning mechanism in the liquid within the pores. Roughened or etched glass surfaces are suggested by Giddings[8,9] to distribute the liquid evenly over the surfaces.

Retention data is widely used in chromatographic studies to extract equilibrium data. Because the retention time for a conservative system (*i.e.*, one without sources or irreversible sinks) is easily written based on a mass balance, the moment method as described here simply conforms with the mass conservation law[3]. However, separation efficiency depends on band spreading, which is quantitatively represented by the second moment, and here the moment technique is of critical importance because of the complex way the transport coefficients appear in μ_2'.

Effect of liquid load on column efficiency

Following the usual procedure[10] we evaluate column efficiency with the expression for the HETP, which is given by:

$$h = L\mu_2'/(\Delta\mu_1)^2 \tag{27}$$

Substituting expressions for first and second moments into the above equation gives us:

$$h = A + B/u + Cu \tag{28}$$

where

$$A = \mu'_2 (0) u^2/L (1 + \delta_0)^2 \tag{29}$$

$$B = 2D_0/\alpha \tag{30}$$

$$C = 2 (\delta_1 + \delta_2)/(1 + \delta_0)^2 \tag{31}$$

Here we have considered the axial dispersion coefficient to be independent of velocity so that eqn. 28 for h has the standard form. More sophisticated representations for D_0 as a function of u are easily implemented[10].

It is easy to verify that the h vs. liquid phase percentage curve has a minimum HETP decreases for low liquid coverage, but a higher liquid percentage leads to an increase in resistance to mass transfer, thus C increases. Optimal liquid phase load will depend on the sample size: at a large sample size A is dominant and one should use a column packing with higher liquid phase concentration. For components retarded longer in the column, and at a higher flow-rate, C is dominant and one should use a column packing with lower liquid phase concentration[11]. The shape of the right-hand branch of the h vs. u curve varies with the liquid/solid ratio, i.e., there is a steady increase in the slope of the right-hand branch of the curve as the amount of the liquid is increased[12] (i.e., the C term increases as the liquid load increases).

LIST OF SYMBOLS

A_s	Particle surface area per unit volume, in contact with gas
c	Concentration of solute in interparticle void
c_i	Concentration of solute in intraparticle voids
c_l	Concentration of solute in liquid film
c_0	Concentration of solute at column entrance
D_i	Effective intraparticle diffusion coefficient
D_0	Effective axial dispersion
h	Height equivalent to a theoretical plate (HETP)
k_a	Adsorption rate constant
k_f	Gas mass transfer coefficient external to particles
$K = c_l/c_i$	Equilibrium partition coefficient
K_a	Adsorption equilibrium constant
r	Radial coordinate inside particle
R	Radius of particles
t	Time
t_R	Retention time
$u_0 = \alpha u$	Superficial velocity
V_l	Volume of liquid per volume of particle
z	Axial distance
α	Column void fraction

β	Particle porosity
μ_1	Normalized first temporal moment
μ'_2	Normalized second central moment

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