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THEORY OF CONSECUTIVE PULSE SAMPLE FEED ELUTION CHROMATOGRAPHY

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SUMMARY

Moments analysis was used to characterize the elution chromatographic peak from a column, in which the longitudinal dispersion in the mobile phase, the radial dispersion inside the porous spherical bed packing and the sorption on the internal surface of the spherical bed packing are simultaneously taking place. A sample feed and an elution step are fed into the column as a consecutive pulse alternately, so that a continuous operation of chromatography can be performed.

INTRODUCTION

The present paper describes a theory of consecutive pulse sample feed elution chromatography which simultaneously takes into account the longitudinal dispersion in the mobile phase, the radial dispersion inside the porous spherical bed packing, and the sorption on the internal surface of the spherical bed packing. The theory is a modification of Kučera's¹ linear non-equilibrium elution chromatography by changing a customarily used injection feed represented by a δ -function to a square pulse train sequence, so that a sample feed and an elution step can be alternated consecutively for an automated continuous operation of chromatography.

FORMULATION OF PROBLEMS

We consider an infinitely long column with a section uniformly filled with the porous spherical bed packing material. The void volume fraction in the column is designated as ϵ_m and the porosity of spherical radius R packing material is ϵ_s . The velocity profile of the mobile phase was assumed to be a plug flow with the average carrier velocity U . The dispersion in the mobile phase was assumed to be in a longitudinal direction only and its dispersion coefficient, D_m , was also assumed to be a constant. Then the solute transfer into the stationary phase through the interphase layer by a mass transfer process with a constant mass transfer coefficient k_M . The solute dispersed further in the stationary phase into the interior of each spherical packing with a constant dispersion coefficient D_s . Finally, on those porous spherical

packings adsorption and desorption were taking place for the solute component. Then the elution will proceed. The equations describing the above chromatographic process are characterized by the following mass balance equations

$$\frac{\partial C_m}{\partial t} + U \frac{\partial C_m}{\partial z} - D_m \frac{\partial^2 C_m}{\partial z^2} + k_M(KC_m - C_s |_{r=R}) = 0 \quad (1)$$

for the mobile phase, and

$$\frac{\partial C_s}{\partial t} - D_s \left(\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right) = - \frac{\partial n}{\partial t} \quad (2)$$

for the stationary phase. Assuming a finite rate of adsorption on the internal porous surface of spherical bed packing with a linear isotherm, one has

$$\frac{\partial n}{\partial t} = k_A C_s - k_D n \quad (3)$$

for adsorption kinetics. C denotes the solute concentration, and subscripts m and s denote mobile and stationary phases, respectively. n is the solute concentration adsorbed on the porous surface. K is the partition coefficient of the solute, and k_A and k_D are the rate constants for adsorption and desorption, respectively.

The initial and boundary conditions for the pulse sample feed train are

$$C_m(z, t) = 0 \quad \text{for } t = 0 \quad (4)$$

$$C_s(r, z, t) = 0 \quad \text{for } t = 0 \quad (5)$$

$$n(r, z, t) = 0 \quad \text{for } t = 0 \quad (6)$$

$$C_m(z, t) = C_0[u(t) - u(t - t_0)] \quad \text{for } z = 0 \quad (7)$$

$$C_m(z, t) = 0 \quad \text{for } z = \infty \quad (8)$$

$$\varepsilon_m k_M(KC_m - C_s |_{r=R}) = - \frac{3(1-\varepsilon_m)\varepsilon_s}{R} \cdot D_s \frac{\partial C_s}{\partial r} \Big|_{r=R} \quad \text{for } r = R \quad (9)$$

$$\frac{\partial C_s}{\partial r} \Big|_{r=0} = 0 \quad \text{for } r = 0 \quad (10)$$

where $u(t)$ is a unit pulse function, t_0 is the time required for one sample leading into the packed section of the column and the expression $3(1 - \varepsilon_m) \cdot \varepsilon_s/R$ gives the surface area of a spherical porous particle per unit volume of the column.

THE LAPLACE TRANSFORMS AND MOMENTS ANALYSIS

Ideally, one would like to obtain an exact solution of $C_m(z, t)$. The set of differential equations subjecting to those initial and boundary conditions is difficult to solve analytically. However, the chromatographic peak can be completely charac-

terized by the statistical moments²⁻⁷. The moments of $C_m(z,t)$ can be found by using either the Laplace or the Fourier transformation. In the Laplace domain the equations describing the system presented above are given as

$$s\bar{C}_m + U \frac{d\bar{C}_m}{dz} - D_m \frac{d^2\bar{C}_m}{dz^2} + k_M(K\bar{C}_m - \bar{C}_s |_{r=R}) = 0 \quad (11)$$

$$s\bar{C}_s - D_s \left(\frac{d^2\bar{C}_s}{dr^2} + \frac{2}{r} \frac{d\bar{C}_s}{dr} \right) = -s\bar{n} \quad (12)$$

$$s\bar{n} = k_A\bar{C}_s - k_D\bar{n} \quad (13)$$

The initial conditions, eqns. 4-6, were used in obtaining those transformations. The boundary conditions in the Laplace domain are

$$\bar{C}_m(0,s) = C_0 \left(\frac{1}{s} - \frac{e^{-r_0s}}{s} \right) \quad (14)$$

$$\bar{C}_m(\infty,s) = 0 \quad (15)$$

$$\varepsilon_m k_M (K\bar{C}_m - \bar{C}_s |_{r=R}) = - \frac{3(1-\varepsilon_m)\varepsilon_s}{R} \cdot D_s \frac{d\bar{C}_s}{dr} \Big|_{r=R} \quad (16)$$

$$\frac{d\bar{C}_s}{dr} \Big|_{r=0} = 0 \quad (17)$$

Elimination of \bar{n} from eqns. 12 and 13 gives

$$\frac{d^2\bar{C}_s}{dr^2} + \frac{2}{r} \frac{d\bar{C}_s}{dr} - \alpha\bar{C}_s = 0 \quad (18)$$

in which

$$\alpha = \frac{1}{D_s} \left[\frac{s^2 + (k_A + k_D)s}{s + k_D} \right] \quad (19)$$

The solution of eqn. 18 together with the boundary conditions eqns. 16 and 17 is obtained as

$$\bar{C}_s = A_1 \cdot \bar{C}_m [\alpha^{\frac{1}{2}}r]^{-\frac{1}{2}} \cdot I_{\frac{1}{2}}(\alpha^{\frac{1}{2}}r) \quad (20)$$

where

$$A_1 = \frac{k_M K \varepsilon_m R^2 [\alpha^{\frac{1}{2}}R]^{\frac{1}{2}}}{3(1-\varepsilon_m)\varepsilon_s D_s \alpha^{\frac{1}{2}} R I_{3/2}(\alpha^{\frac{1}{2}}R) + k_M \varepsilon_m R^2 I_{\frac{1}{2}}(\alpha^{\frac{1}{2}}R)} \quad (21)$$

Substituting eqn. 20 into eqn. 11, one obtains

$$\frac{d^2\bar{C}_m}{dz^2} - \frac{U}{D_m} \frac{d\bar{C}_m}{dz} - \frac{A_2}{D_m} \bar{C}_m = 0 \quad (22)$$

in which

$$A_2 = s + \frac{3k_M K(1 - \varepsilon_m)\varepsilon_s D_s \alpha^{\pm} R I_{3/2}(\alpha^{\pm} R)}{3(1 - \varepsilon_m)\varepsilon_s \alpha^{\pm} R I_{3/2}(\alpha^{\pm} R) + k_M \varepsilon_m R^2 I_{\frac{1}{2}}(\alpha^{\pm} R)} \quad (23)$$

The solution for \bar{C}_m with the boundary conditions, eqns. 14 and 15, is

$$\bar{C}_m(z,s) = C_0 \frac{1 - e^{-t_0 s}}{s} \exp \left\{ \frac{U}{2D_m} - \left[\frac{U}{2D_m} + \frac{A_2}{D_m} \right] z \right\} \cdot z \quad (24)$$

Since we are interested in $\bar{C}_m(z,s)$ at a particular point L (at the exit of the column) we can replace z in eqn. 24 by L . It is difficult, if at all possible, to invert the equation back to the time domain. However, the expression similar to Kučera's¹ expansion

$$C_m(t) = C_m(z,t) |_{z=L} = \sum_{n=0}^{\infty} a_n H_n \left(\frac{t - \bar{\mu}_1}{\sqrt{2\mu_2}} \right) \exp \left[- \frac{(t - \bar{\mu}_1)^2}{2\mu_2} \right] \quad (25)$$

can be found by using Hermite polynomials⁷

$$H_n(x) = \sum_{j=0}^N \frac{(-1)^j n!}{j!(n-2j)!} \cdot (2x)^{n-2j} \quad (26)$$

where $N = n/2$ for even n ; $N = (n-1)/2$ for odd n . The expansion coefficients a_n are given by the equation

$$a_n = \frac{1}{2^n n! \sqrt{\pi}} \int_0^{\infty} C_m(t) H_n \left(\frac{t - \bar{\mu}_1}{\sqrt{2\mu_2}} \right) \frac{dt}{\sqrt{2\mu_2}} \quad (27)$$

based on the orthogonality of Hermite polynomials. In eqns. 25 and 27, μ_K and $\bar{\mu}_K$ are the K th moment of function $C_m(t)$ defined by the equation

$$\bar{\mu}_K = m_K / m_0 \quad (28)$$

where

$$m_K = \int_0^{\infty} t^K C_m(t) dt \quad (29)$$

For convenience, all moments higher than the first around the center of gravity of $C_m(t)$ are generally used. The K th central moment is defined by

$$\mu_K = \frac{1}{m_0} \int_0^{\infty} (t - \bar{\mu}_1)^K C_m(t) dt = \sum_{i=0}^K \binom{K}{i} (-\bar{\mu}_1)^{K-i} \cdot \bar{\mu}_i; \quad K > 1. \quad (30)$$

By use of the property of the Laplace transform

$$\int_0^{\infty} t^K C_m(t) dt = (-1)^K \lim_{s \rightarrow 0} \frac{\partial^K \bar{C}_m(s)}{\partial s^K} \quad (31)$$

the moments of $C_m(t)$ are obtained. The expansion coefficients a_n expressed in terms of central moments μ_k are

$$a_0 = \frac{m_0}{\sqrt{2\pi\mu_2}} \quad (32)$$

$$a_1 = a_2 = 0 \quad (33)$$

$$a_n = \frac{m_0}{\sqrt{2\pi\mu_2}} \sum_{j=0}^n \frac{(-1)^j \mu_{n-2j} \mu_2^j}{j!(n-2j)! 2^j (2\mu_2)^{\frac{n}{2}}} \quad (34)$$

The resulting moments up to the third central moments are presented by

$$\mu_0 = \bar{\mu}_0 = 1 \quad (35)$$

$$\mu_1 = 0; \quad \bar{\mu}_1 = \frac{t_0}{2} + \frac{L}{U} (1 + \varphi) \quad (36)$$

where

$$\varphi = \frac{K(1 - \varepsilon_m)\varepsilon_s(k_A + k_D)}{\varepsilon_m k_D} \quad (37)$$

$$\mu_2 = \frac{t_0}{12} + \frac{2D_m L}{U^3} (1 + \varphi)^2 + \frac{L}{U} \left[\frac{13\varphi^2}{10k_M K} + \frac{13R^2 \varepsilon_m \varphi^2}{160K \varepsilon_s D_s (1 - \varepsilon_m)} + \frac{2k_A \varphi}{k_D(k_A + k_D)} \right] \quad (38)$$

$$\begin{aligned} \mu_3 = & \frac{12D_m L}{U^5} (1 + \varphi)^3 + \left(\frac{2L^2}{U^2} + \frac{4D_m L}{U^3} \right) (1 + \varphi + \frac{2D_m L}{U^3}) \left[\frac{13\varphi^2}{10k_M K} + \right. \\ & \left. \frac{13\varepsilon_m R^2 \varphi^2}{160K \varepsilon_s (1 - \varepsilon_m) D_s} + \frac{2k_A \varphi}{k_D(k_A + k_D)} \right] + \frac{L}{U} \left[\frac{4137\varphi^3}{640k_M^2 K^2} + \frac{4R^2 \varepsilon_m \varphi^3}{5k_M K^2 \varepsilon_s D_s (1 - \varepsilon_m)} + \right. \\ & \left. \frac{16\varepsilon_m^2 R^4 \varphi^3}{315\varepsilon_s^2 (1 - \varepsilon_m)^2 K^2 D_s^2} + \frac{117k_A \varphi^2}{15k_M k_D (k_A + k_D) K} + \frac{39R^2 \varphi k_A}{80D_s k_D^2} + \frac{16k_A \varphi}{(k_A + k_D)} \right] \quad (39) \end{aligned}$$

DISCUSSION

The first moment as indicated by Grushka *et al.*⁸ is the retention time t_R of the solute, *i.e.*, the time when the maximum concentration is registered at the point of detection. In this case, the retention time is given by

$$t_R = \bar{\mu}_1 = \frac{t_0}{2} + \frac{L}{U} (1 + \varphi) \quad (40)$$

It is interesting to note that t_R is unaffected by the dispersions in the longitudinal direction and in the porous spherical bed packing and that the parameter φ in eqn.

37 is a modification of Kučera's parameter¹ $K(1 - \epsilon_m)/\epsilon_m$ by multiplying with a factor of $\epsilon_s(k_A + k_D)/k_D$. The peak does depend on the bed structure and adsorption and desorption coefficients. Probably, the sequence of pulse sample feed and elution trains eliminates the effect of dispersions, and the kinetic coefficients and the bed structure are becoming more important factors in the process. The result is similar to the one obtained by Grushka⁹, but without assuming the term $2D_m/U^2$ being negligible. The second moment is the peak variance which leads to a direct derivation of the plate height, H .

$$H = \frac{L\mu_2}{\bar{\mu}_1^2} = \frac{2D_m}{U} + \frac{U}{(1+q)^2} \left[\frac{13q^2}{10k_M K \epsilon_s} + \frac{13\epsilon_m R^2 q^2}{160KD_s \epsilon_s} + \frac{2k_A q}{k_D(k_A + k_D)} \right] \quad (41)$$

In obtaining eqn. 41, the loading time t_0 was assumed to be very small compared with the other terms of eqns. 36 and 38. The theoretical plate height depends on all factors characterizing the column, its filling and transport of the given compound through the column. It increases with the increasing coefficient of the longitudinal dispersion, the partition coefficient, and the size of bed packing particles R . It decreases with the increasing of the dispersion coefficient in the porous bed packing, the mass transfer coefficient from the mobile phase to the stationary phase and the porosity of the bed packing.

With the information of t_0 and t_R , one should be able to program the sequence for sample feed-elution schedule for automated continuous operation of the chromatography.

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