

Evaluation of nonlinear chromatographic performance by frontal analysis using a simple multi-plate mathematical model

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Abstract

A multi-plate (MP) mathematical model was proposed by frontal analysis to evaluate nonlinear chromatographic performance. One of its advantages is that the parameters may be easily calculated from experimental data. Moreover, there is a good correlation between it and the equilibrium-dispersive (E-D) or Thomas models. This shows that it can well accommodate both types of band broadening that is comprised of either diffusion-dominated processes or kinetic sorption processes. The MP model can well describe experimental breakthrough curves that were obtained from membrane affinity chromatography and column reversed-phase liquid chromatography. Furthermore, the coefficients of mass transfer may be calculated according to the relationship between the MP model and the E-D or Thomas models.

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1. Introduction

Frontal analysis (FA) is a useful method for chromatographic studies. Compared to another one, the pulse method, FA method is more suited for preparative chromatography where maximum usage of the adsorbent is desirable. Particularly for many preparative affinity separations, the assumption of a linear adsorption isotherm, which derived analytical solutions describing the chromatographic performance, is not applicable. In these cases, FA is usually considered as the preferred method [1–3].

FA has been widely applied to determine adsorption isotherms from breakthrough curves that are obtained at different feed concentrations of the adsorbate [4–9]. As its inverse problem, the breakthrough curve may be predicted when the isotherm is already known. Because the shape of the breakthrough curve can also be influenced by factors such as dispersion and sorption kinetics, this study will provide information about the process and then be helpful to optimize the

operation [3,10,11]. For this purpose, Chase [1] had described a theoretical approach of FA to predict the performance of preparative affinity separations in packed columns. Suen and co-workers [12–14] proposed a mathematical model for FA to analyze the design and operation of affinity membrane bioseparations. Recently, Miyabe and Guiochon [15] proposed a FA method to measure the lumped mass transfer rate coefficient ($k_{m,L}$) in column reversed-phase liquid chromatography.

The equilibrium-dispersive (E-D) [7,15] and Thomas models [1,12,16] have been widely applied to FA. The E-D model lumps all contributions leading to band broadening into an apparent dispersion coefficient, D , and the Thomas model lumps those into an association rate coefficient, k_1 . These coefficients may be used to indicate the chromatographic performance. In practice, D and k_1 may be estimated by comparing experimental curves and theoretical ones that are calculated by changing the values of the coefficients [15]. In some cases, however, this procedure turns out to be arbitrary because there was usually a little discrepancy between experimental and theoretical values [14,15,17,18]. In these cases, some effects for band broadening turn not to be lumped

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into D and k_1 . In addition, solving these models needs numerical methods and it will involve a great number of repeated computations. This makes the work of the calculation be somewhat large, and it seems not to be handy for chromatographers especially without computing ground.

In this paper, we propose a new mathematical model, the multi-plate (MP) model, for the FA method. It is expected to be capable of describing the breakthrough curve and also handy for chromatographers. As validation for its practical use, two different chromatographic systems, column reversed-phase liquid chromatography (RPLC) and membrane affinity chromatography (MAC) were performed. In the former, the E-D model has been widely applied due to the fact that fast equilibrium of the adsorbate between the mobile and stationary phases usually occurs. In the latter, the Thomas model turns out to be more appropriate because the slow sorption kinetics is the limiting factor. By applying the MP model to describe the breakthrough curves obtained in RPLC and MAC, it is shown that this model may be used to obtain information about band broadening effects.

2. Theoretical

2.1. Multi-plate model

In general, the chromatographic process may also be considered as occurring in series of theoretical plates [19]. For the FA method, in each plate, according to that the amount of the solute entering the plate is the sum of that leaving and the increment in mobile and stationary phases, the mass balance equation may be expressed as:

$$C_0 dV - C_1 dV = \frac{V_m(1-\varepsilon)}{N} dC_{s,1} + \frac{V_m\varepsilon}{N} dC_1 \quad (1a)$$

$$C_{i-1} dV - C_i dV = \frac{V_m(1-\varepsilon)}{N} dC_{s,i} + \frac{V_m\varepsilon}{N} dC_i \quad (1b)$$

$$C_{N-1} dV - C_N dV = \frac{V_m(1-\varepsilon)}{N} dC_{s,N} + \frac{V_m\varepsilon}{N} dC_N \quad (1c)$$

where V is the effluent volume, V_m is the volume of the column or membranes, N is the number of theoretical plates, ε is the porosity, C and C_s are the solute concentration in the mobile and stationary phases, respectively. The number in the subscript denotes the index of theoretical plates.

By summing up above equations, we obtain:

$$C_0 - C_N = \frac{V_m(1-\varepsilon)}{N} \sum_{i=1}^N \frac{dC_{s,i}}{dV} + \frac{V_m\varepsilon}{N} \sum_{i=1}^N \frac{dC_i}{dV} \quad (2)$$

Because the inlet concentration is kept constant, the change rate of solute concentration in the mobile and stationary phases in each plate, dC_i/dV and $dC_{s,i}/dV$, may be assumed to decrease to zero with increasing effluent volume. From a certain time when the adsorption in the first several plates reaches saturation, the breakthrough curve may mainly re-

fect the process in the last plate. In this case, Eq. (2) may be simplified as:

$$C_0 - C_N \approx \frac{V_m(1-\varepsilon)}{N} \frac{dC_{s,N}}{dV} + \frac{V_m\varepsilon}{N} \frac{dC_N}{dV} \quad (3)$$

If the equilibrium of the solute between the mobile and stationary phases may be accounted for by Langmuir isotherm,

$$C_s = \frac{C_1 C}{K_d + C} \quad (4)$$

we obtain:

$$C_{s,N} = \frac{C_1 C_N}{K_d + C_N},$$

$$\frac{dC_{s,N}}{dV} = \frac{dC_{s,N}}{dC_N} \frac{dC_N}{dV} = \frac{C_1 K_d}{(K_d + C_N)^2} \frac{dC_N}{dV} \quad (5)$$

By substituting Eq. (5) into Eq. (3), we obtain:

$$C_0 - C_N = \frac{V_m(1-\varepsilon)}{N} \frac{C_1 K_d}{(K_d + C_N)^2} \frac{dC_N}{dV} + \frac{V_m\varepsilon}{N} \frac{dC_N}{dV} \quad (6)$$

Eq. (6) may be rewritten as:

$$\begin{aligned} \frac{dV}{V_m(1-\varepsilon)} &= \frac{C_1 K_d}{N} \frac{dC_N}{(C_0 - C_N)(K_d + C_N)^2} \\ &+ \frac{\varepsilon}{N(1-\varepsilon)} \frac{dC_N}{C_0 - C_N} \\ &= \frac{C_1 K_d}{N(C_0 + K_d)} \frac{dC_N}{(K_d + C_N)^2} \\ &+ \frac{C_1 K_d}{N(C_0 + K_d)^2} \frac{dC_N}{K_d + C_N} \\ &+ \frac{1}{N} \left[\frac{C_1 K_d}{(C_0 + K_d)^2} + \frac{\varepsilon}{1-\varepsilon} \right] \frac{dC_N}{C_0 - C_N} \quad (7) \end{aligned}$$

Eq. (7) is an ordinary differential equation. With initial condition $C_N = 0$ at $V = 0$, the analytical solution of it is:

$$\begin{aligned} \frac{V}{V_m(1-\varepsilon)} &= \frac{C_1}{N(C_0 + K_d)} \frac{C_N}{K_d + C_N} \\ &+ \frac{C_1 K_d}{N(C_0 + K_d)^2} \ln \left(1 + \frac{C_N}{K_d} \right) \\ &- \frac{1}{N} \left[\frac{C_1 K_d}{(C_0 + K_d)^2} + \frac{\varepsilon}{1-\varepsilon} \right] \ln \left(1 - \frac{C_N}{C_0} \right) \quad (8) \end{aligned}$$

If C replaces C_N to denote the outlet concentration and the following dimensionless groups are introduced to simplify the expressions,

$$c = \frac{C}{C_0} \quad (9a)$$

$$\lambda = \frac{C_1}{C_0} \quad (9b)$$

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