



Moment equations for chromatography based on Langmuir type reaction kinetics



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ABSTRACT

Moment equations were derived for chromatography, in which the reaction kinetics between solute molecules and functional ligands on the stationary phase was represented by the Langmuir type rate equation. A set of basic equations of the general rate model of chromatography representing the mass balance, mass transfer rate, and reaction kinetics in the column were analytically solved in the Laplace domain. The moment equations for the first absolute moment and the second central moment in the real time domain were derived from the analytical solution in the Laplace domain. The moment equations were used for predicting the chromatographic behavior under hypothetical HPLC conditions. The influence of the parameters relating to the adsorption equilibrium and to the reaction kinetics on the chromatographic behavior was quantitatively evaluated. It is expected that the moment equations are effective for a detailed analysis of the influence of the mass transfer rates and of the Langmuir type reaction kinetics on the column efficiency.

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1. Introduction

Solute band spreads in a column due to mass transfer phenomena and intermolecular interactions between solute molecules and functional ligands on the stationary phase. This means that the kinetic information about the intermolecular interactions, i.e., association rate constant (k_a) and dissociation rate constant (k_d), can be obtained by analyzing the band spreading in chromatography. Additionally, information about chemical equilibrium of the intermolecular interactions, i.e., association equilibrium constant (K_A) and dissociation equilibrium constant (K_D), can also be obtained because $K_A = k_a/k_d$ and $K_D = 1/K_A$.

Kinetic studies on intermolecular interactions have been carried out by using various types of chromatographic systems. One of the strategies for deriving k_d is the peak profiling method, which is based on the comparison of the elution peak of a retained compound and that of a non-retained one [1]. Different types of intermolecular interactions were studied by using affinity chromatography between proteins and drugs [2–4] and between concanavalin A and one type of sugar [5,6]. The plate height equation developed by Horvath and Lin was used in the peak profiling method [7,8]. However, the formulae of the moment equations for

first absolute moment (μ_1) and second central moment (μ_2') of elution peaks were not reported. They proposed only the plate height equation.

Other method was also used for studying the reaction kinetics in chromatography, i.e., non-linear chromatography [9–16]. In this case, chromatographic data were analyzed on the basis of an equation representing the correlation between the ratio of the concentration of a solute in the mobile phase to that injected into the column and the ratio of time to the hold-up time. The equation was derived by solving the basic equations concerning the mass balance of the solute compound and the Langmuir type reaction kinetics under some boundary conditions. However, in the non-linear chromatography, the contribution of several mass transfer processes in the column to band broadening, such as eddy diffusion, external mass transfer, and pore and surface diffusion in the stationary phase, was not considered. In addition, it was also pointed out for the non-linear chromatography that the possible presence of band broadening due to the concentration dependence behavior leads to the underestimation of the analytical results [4].

Other chromatographic methods, i.e., peak decay method and breakthrough experiment, were also used for the kinetic studies on the intermolecular interactions between concanavalin A and a fluorescent sugar [17] and between staphylococcal enterotoxin B and one type of peptide [18].

The moment analysis method based on the general rate model of chromatography is one of the strategies for deducing the

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information about the retention equilibrium and the mass transfer and reaction kinetics in the column from μ_1 and μ_2' of elution peaks experimentally measured [19–25]. It is expected that kinetics information about intermolecular interactions can be more accurately obtained by the moment method because band broadening in chromatography due to several mass transfer processes in the column and in the stationary phase is analyzed in more detail by the moment method.

The first goal of this study is to develop new moment equations for chromatography, in which the reaction kinetics between solute molecules and functional ligands is represented by the Langmuir type rate equation. Moment equations previously reported were usually developed by assuming adsorption–desorption phenomena at real adsorption sites on the stationary phase surface as the reaction kinetic process in chromatography. Its driving force is the difference between the real solute concentration in the mobile phase and the concentration equilibrium to the amount of the solute adsorbed on the stationary phase.

The second goal is to discuss the influence of some parameters of the Langmuir type reaction on chromatographic performance. The new moment equations proposed in this study were used to predict the chromatographic behavior under hypothetical HPLC conditions. The calculated results under some different conditions were compared from the retention behavior, band broadening, and column efficiency.

2. Derivation of moment equations

On the basis of the general rate model of chromatography, moment equations had already been developed about 40–50 years ago for the chromatographic processes in the column packed with full-porous spherical particles [26–32]. However, recently, various separation media had been developed for fast HPLC with high efficiency, e.g., monoliths and core-shell particles. Their structural characteristics are quite different from those of full-porous spherical particles. Therefore, a series of moment equations for the various separation media have also been developed [33–36]. It was tried to construct a framework of moment equations for studying chromatographic behavior in detail.

In this study, new moment equations were derived as follows. Basic equations representing the mass balance, mass transfer, and reaction kinetics in the column and in the stationary phase were solved in the Laplace domain. In the basic equations, the reaction kinetics between solute molecules and functional ligands on the stationary phase surface was represented by the Langmuir type equation. The new moment equations in the time domain were derived from the analytical solution of the basic equations in the Laplace domain.

2.1. Fundamental assumptions for deriving moment equations

The moment equations were derived on the basis of the following set of assumptions.

- (1) Chromatographic processes proceed under linear isotherm conditions.
- (2) The column is radially homogenous. There is no diffusion of solute molecules in the radial direction of the column.
- (3) The column is controlled under isothermal conditions.
- (4) The stationary phase spherical particles consist of a solid part and mesopores. They are homogeneous. The radii of the particles and mesopores are constant.
- (5) The mobile phase solvent flows through the external pore space. It is not adsorbed on the stationary phase.

- (6) The mobile phase is incompressible. No parameter, such as the coefficients of the isotherm and the mobile phase viscosity, has pressure dependence.
- (7) The partial molar volume of the solute is constant.

2.2. Basic equations

The partially differential equations, Eqs. (1)–(4), based on the general rate model of chromatography represent the mass balance, the mass transfer rate, and the chemical reaction kinetics of solute molecules in the column and in the stationary phase.

$$D_L \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{A_s}{\varepsilon_e} N_0 = \frac{\partial C}{\partial t} \quad (1)$$

$$N_0 = k_f(C - C_{i,R}) = D_e \left(\frac{\partial C_i}{\partial r} \right)_R \quad (2)$$

$$D_e \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) - N_i = \varepsilon_i \frac{\partial C_i}{\partial t} \quad (3)$$

$$N_i = (1 - \varepsilon_i) \frac{\partial q}{\partial t} = (1 - \varepsilon_i)[k_a C_i(q_{st} - q) - k_d q] \quad (4)$$

Equation (4) is written as follows when q is negligibly smaller than q_{st} . This means that chromatographic experiments must be carried out under sufficiently low concentration conditions. However, the moment equations are also effective under linear (Henry type) isotherm conditions. Both the conditions are not contradictory with each other.

$$N_i = (1 - \varepsilon_i) \frac{\partial q}{\partial t} = (1 - \varepsilon_i)[k_a C_i q_{st} - k_d q] \quad (5)$$

where C is the concentration of the solute in the bulk mobile phase, z the longitudinal distance along the column, t the time, D_L the axial dispersion coefficient, u the average interstitial velocity of the mobile phase, A_s the ratio of the total external surface area of the stationary phase to the column volume, ε_e the column void fraction (external porosity), N_0 the mass flux of the solute molecule from the bulk mobile phase to the external surface of the stationary phase, C_i the concentration of the solute molecule within the mesopores in the stationary phase, R the radius of the stationary phase spherical particles, r the radial distance from the center of the stationary phase spherical particles, k_f the external mass transfer coefficient, D_e the effective diffusion coefficient of the solute molecule in the stationary phase, N_i the mass flux of the solute molecule from the stagnant mobile phase in the mesopore space to the surface of the solid part of the stationary phase, ε_i the porosity of the stationary phase particles (internal porosity), k_a the association rate constant, k_d the dissociation rate constant, q is the amount of the solute molecule adsorbed on the stationary phase, and q_{st} the saturated amount of the solute adsorbed.

The initial and boundary conditions are as follows.

$$C(z, t = 0) = 0 \quad \text{for } 0 \leq z \leq L \quad (6)$$

$$C_i(z, t = 0, r) = 0 \quad \text{for } 0 \leq z \leq L, 0 \leq r \leq R \quad (7)$$

$$q(z, t = 0) = 0 \quad \text{for } 0 \leq z \leq L \quad (8)$$

$$C(z = 0, t) = C_0 \quad \text{for } 0 \leq t \leq \tau \quad (9)$$

$$C(z = 0, t) = 0 \quad \text{for } \tau \leq t \quad (10)$$

$$k_f(C - C_{i,r=R}) = D_e \left(\frac{\partial C_i}{\partial r} \right)_{r=R} \quad (11)$$

$$\left(\frac{\partial C_i}{\partial r} \right)_{r=0} = 0 \quad (12)$$

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