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Analytical solutions and moment analysis of general rate model for linear liquid chromatography

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HIGHLIGHTS

- The linear general rate model (GRM) is analyzed for different boundary conditions.
- The first four moments of the model are analytically and numerically calculated.
- Relationships are derived to match moments of GRM and the lumped kinetic model (LKM).
- These relations can be used to estimate parameters of LKM from GRM parameters.
- The finite volume scheme is applied to validate the analytical results.

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ABSTRACT

The general rate model (GRM) is considered to be a comprehensive and reliable mathematical model for describing the separation and mass transfer processes of solutes in chromatographic columns. However, the numerical solution of model equations is complicated and time consuming. This paper presents analytical solutions of the GRM for linear adsorption isotherms and different sets of boundary conditions at the column inlet and outlet. The analytical solutions are obtained by means of the Laplace transformation. Numerical Laplace inversion is used to transform back the solution in the time domain because analytical inversion cannot be obtained. The first four temporal moments are derived analytically using the Laplace domain solutions. The moments of GRM are utilized to analyze the retention times, band broadenings, front asymmetries and kurtosis of the elution profiles. Relationships are derived among the kinetic parameters to match the first four moments of GRM and the simpler lumped kinetic model (LKM). For validation, the analytical solutions are compared with numerical solutions of a second order finite volume scheme. Good agreements in the results verify the correctness of analytical solutions and the accuracy of the numerical scheme.

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1. Introduction

Column liquid chromatography is one of the most versatile separation techniques. It is widely used for analysis and purification in several industries aiming to produce pharmaceuticals, food, and fine chemicals. The concept is successfully applied to perform numerous difficult separation processes, for instance the separation of enantiomers and the isolation of specific proteins from fermentation broths. In the column liquid chromatography, a mobile phase percolates through a bed of fixed porous particles, carrying the mixture components which interact differently with the stationary phase. Components interacting strongly with the particles will be transported (elute) slowly along the column as compared to the components with weaker interactions. Therefore, each component will form a concentration band profile moving with a specific velocity in the column. These velocity differences make possible, for long enough columns, to collect pure fractions of components at the outlet of the column.

Mathematical modeling of chromatographic processes is useful for understanding and analyzing dynamic composition fronts in chromatographic columns without extensive experiments. Different mathematical models with different degrees of complexity describing the mass transfer and partition processes are available in the literature. The most important of these models are the general rate model (GRM), the lumped kinetic model (LKM), the

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equilibrium-dispersive model (EDM), and the ideal model of chromatography, see e.g. Guiochon (2002), Guiochon and Lin (2003), Guiochon et al. (2006), Ruthven (1984), and Carta (1988).

The EDM assumes that the mass transfer is of infinite rate. The LKM incorporates with the rate of variation of the local concentration of solute in the stationary phase and local deviation from equilibrium concentrations. The analytical solutions and moment analysis of these models are already presented in detail in our previous publications (Javeed et al., 2013; Qamar et al., 2013). In this paper, the analysis of GRM is our main concern.

The GRM is considered to be a very comprehensive model and has the potential to achieve an accurate description of chromatographic profiles. It incorporates several important factors of the mass transfer process in the column, such as the axial dispersion, external mass transfer resistance, pore diffusion and surface diffusion.

In this work, the analytical solutions of GRM are obtained for different sets of boundary conditions considering a single component fluid. The model equations are solved by using the Laplace transformation. Moment analysis has been comprehensively discussed in the literature, see for example Kubin (1965a,b), Kucera (1965), Schneider and Smith (1968), Suzuki (1973), Wolff et al. (1980a,b), Ruthven (1984), Lenhoff (1987), Antos et al. (2003), Guiochon et al. (2006), Miyabe and Guiochon (2000, 2003), Miyabe (2007, 2009) and Javeed et al. (2013). In these partly classical papers analytical expressions have been generated for specific chromatographic models and boundary conditions. The analysis typically covered just the most important first and second moments, i.e. retention times and band broadening. In a few studies also the third moment, which describes peak and front asymmetries, was derived and evaluated. In the present paper we address several aspects that have not been treated in detail up to now. We will derive and compare also the fourth moment, i.e. the kurtosis or flatness. Using low-noise detectors and complete capture of the responses this moment appears to be still experimentally accessible. Since the influence of the boundary conditions is often not discussed in sufficient depth, we will further compare the moment expressions for Danckwerts and Dirichlet conditions considering both rectangular pulses and steps as inlet profiles. In order to compare quantitatively the first four moments of GRM and LKM are derived. With this analysis it is intended to elucidate the connections between the specific kinetic parameters, including for the first time the results for the fourth moments. Finally, going beyond previous studies, we will provide a comparison of the analytically derived moments with moments calculated independently by integrating numerically calculated effluent profiles. For this advanced high resolution methods are applied (Javeed et al., 2011a, 2011b), which are capable to treat also the more general case of nonlinear equilibria.

The structure of the paper is as follows: The GRM is described in Section 2. Section 3 presents the derivation of analytical solutions and moments of the GRM. Numerical test problems are presented in Section 4. Concluding remarks are given in Section 5.

2. The general rate model (GRM)

The GRM considers, besides functions for the distribution equilibria, several contributions of mass transfer processes occurring in chromatography which cause band broadening. More specifically, axial dispersion, mass transfer between mobile and stationary phases and intraparticle pore diffusion are included in the mass balance equations. Limiting finite rates of adsorption–desorption is sometimes also included but not considered below. Thus, the GRM contains two mass balances for each solute, one for the column and one for the particles of stationary phase.

The mass balance for a single solute component percolating through a column filled with spherical particles of radius R_p is given as

$$\frac{\partial c}{\partial t}+u\frac{\partial c}{\partial z}=D_L\frac{\partial^2 c}{\partial z^2}-\frac{3}{R_p}Fk_{ext}(c-c_p(r=R_p)). \tag{1}$$

In the above equation, c and c_p are the concentrations of a solute in the bulk of the fluid and in particle pores, respectively. The phase ratio F is defined as $F=(1-\varepsilon)/\varepsilon$, where ε is the external porosity. Moreover, u is the interstitial velocity, D_L represents the axial dispersion coefficient, k_{ext} is the external mass transfer coefficient, and t and z denote the time and axial coordinate of the column, respectively. In addition, r is the radial coordinate of spherical particles of radius R_p.

The mass balance equation for the solute in the stationary phase can be expressed assuming two mechanisms of intraparticle transport:

$$\varepsilon_p\frac{\partial c_p}{\partial t}+(1-\varepsilon_p)\frac{\partial q^*}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left[\varepsilon_p D_p\frac{\partial c_p}{\partial r}+(1-\varepsilon_p)D_s\frac{\partial q^*}{\partial r}\right]\right), \tag{2}$$

where q^* is the local concentration of solute in the stationary phase, ε_p is the internal porosity, D_p is the pore diffusivity, and D_s is the surface diffusivity.

Eqs. (1) and (2) are connected at $r=R_p$ via the following expression which quantifies the temporal change of the average loading of the particles:

$$\left[\varepsilon_p D_p\frac{\partial c_p}{\partial r}+(1-\varepsilon_p)D_s\frac{\partial q}{\partial r}\right]_{r=R_p}=k_{ext}(c-c_p|_{r=R_p}). \tag{3}$$

The initial condition of Eq. (1) for an initially regenerated column is given as

$$c(0,z)=0 \quad (0<z<L), \tag{4}$$

and initial conditions of Eq. (2) considering empty particles are given as

$$q^*(0,z,r)=0, \quad c_p(0,z,r)=0. \tag{5}$$

Because rapid adsorption or desorption rates are assumed, the concentrations of solute in the pores and that in the stationary phase are in the state of equilibrium.

Only linear adsorption isotherms are considered in this work:

$$q^*=ac_p. \tag{6}$$

By using Eq. (6), the right hand side term in the square brackets of Eq. (2) can be simplified as

$$\varepsilon_p D_p\frac{\partial c_p}{\partial r}+(1-\varepsilon_p)D_s\frac{\partial q^*}{\partial r}=D_{eff}\frac{\partial c_p}{\partial r}, \tag{7}$$

where

$$D_{eff}=\varepsilon_p D_p+(1-\varepsilon_p)D_s a. \tag{8}$$

Thus, in linear form, Eq. (2) can be rewritten as

$$a^*\frac{\partial c_p}{\partial t}=\frac{D_{eff}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_p}{\partial r}\right), \tag{9}$$

with

$$a^*=\varepsilon_p+(1-\varepsilon_p)a. \tag{10}$$

Similarly, Eq. (3) simplifies to

$$D_{eff}\frac{\partial c_p}{\partial t}\Big|_{r=R_p}=k_{ext}(c-c_p|_{r=R_p}). \tag{11}$$

Moreover, appropriate inlet and outlet boundary conditions (BCs) are required for Eqs. (1) and (2).

The following two types of boundary conditions are considered for Eq. (1).

Boundary conditions of type I: *Robin* (*or Danckwerts*) *type inlet BCs*. In this case, the Robin type boundary condition, known in

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