Numerical approximation of nonlinear and non-equilibrium two-dimensional model of chromatography

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ABSTRACT

This article is concerned with the numerical approximation of a nonlinear model describing the two-dimensional non-equilibrium transport of multi-component mixtures in a chromatographic column of cylindrical geometry. In contrast to previous studies, the work includes joint analysis of deviations from equilibrium and the possibility that radial concentration profiles can develop. The considered radial gradients are typically ignored, which can be problematic in the case of non perfect injections. The model consists of nonlinear convection-diffusion partial differential equations coupled with some differential and algebraic equations. A high resolution finite volume scheme is applied to solve the model equations numerically. The considered case studies include single-component, two-component and three-component elution on fixed (non-movable) beds of liquid chromatography. The developed numerical algorithm is an efficient tool to study the effects of mass transfer kinetics on the elution profiles.

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1. Introduction

Chromatography, originated as a preparative separation technique, is one of the greatest methodical phenomena available to the modern analysts. This technique is successfully employed to target complex separation tasks, which demand high purity of the product for many types of mixtures (Guiochon and Lin, 2003; Guiochon, 2002; Guiochon et al., 2006; Ruthven, 1984). Application areas of chromatography include (a) purification of the reactant mixtures in chemical synthesis, (b) purification of bio-chemicals such as proteins for bio-pharmaceutical industry, (c) analysis of sample mixtures in forensics, such as body fluids and bio-chemicals, and (d) analysis of environmental samples (Guiochon and Lin, 2003; Guiochon, 2002; Guiochon et al., 2006; Ruthven, 1984).

Chromatographic methods are based on selective adsorption of mixture compounds on a solid phase (or liquid phase) with high surface area. In liquid–solid column chromatography, a mobile (liquid) phase, carrying mixture components is passed through a tabular column containing the stationary (solid) phase. During migration, each component of the mixture interacts to varying degrees with the stationary phase. Thus, components of the mixture

are continuously partitioned between solid (adsorbent) and mobile phases. Components having strong interaction with the stationary phase propagate slowly along the column compared to the weakly interacting components. A complete separation of the components can be achieved if the column length is long enough (Guiochon et al., 2006; Ruthven, 1984).

The dynamical behavior of chromatographic columns can be illustrated by several different types of models. These models include the equilibrium dispersive model (EDM), the non-equilibrium lumped kinetic model (LKM) and the general rate model (GRM) (Guiochon and Lin, 2003; Guiochon, 2002; Guiochon et al., 2006; Ruthven, 1984). All models essentially consider nonlinear convection-dominated partial differential equations (PDEs) coupled with some differential or algebraic equations. This article deals with the nonlinear two-dimensional lumped kinetic model (2D-LKM) of chromatography. Analytical solutions are possible under linear adsorption conditions only. Therefore, accurate, stable and computationally efficient numerical methods are needed for determining adsorption dynamics inside chromatographic columns (Guiochon et al., 2006; Javeed et al., 2011a; von Lieres and Andersson, 2010). Generally, chromatographic processes can be simulated by three well known numerical methods namely, the finite difference, the finite element, and the finite volume methods (Guiochon et al., 2006; Javeed et al., 2011a,b; Püttmann et al., 2014, 2016; Qamar et al., 2016; Rouchon et al., 1987). Sharp

discontinuities and steep concentration fronts are the fundamental features of nonlinear convection-diffusion partial differential equations. Hence, an efficient numerical techniques are needed to capture the sharp discontinuities in the profiles accurately at correct position (Guiochon et al., 2006; Javeed et al., 2011a; Leer, 1977; LeVeque, 1992).

The finite volume method (FVM) have been widely applied to simulate different chromatographic processes and were found to be a good choice for the numerical simulation of such nonlinear convection dominated problems (Cruz et al., 2005; Javeed et al., 2011a; von Lieres and Andersson, 2010; Webley and He, 2000). The FVM was initially introduced for nonlinear hyperbolic equations which is based upon three main features namely, formal integration, discretization and solution. Such types of schemes are stable and high order accurate on coarse grids. The technique resolve sharp variations by avoiding numerical oscillations and over-predictions in the solutions (Leer, 1977; LeVeque, 1992; Koren, 1993).

This study extends and generalizes our recent study for linear 2D-LKM (Parveen et al., 2015) to nonlinear 2D-LKM. The one-dimensional (1D) high resolution finite volume scheme (HR-FVS) of Koren (Javeed et al., 2011a; Koren, 1993) is extended to solve the current 2D-model equations. The scheme is second order accurate in the axial and radial-coordinates. The resulting system of ordinary differential equations (ODEs) is solved by using a second-order Runge-Kutta (RK) method. The considered RK-method is total variation bounded (TVB) which preserves the non-negativity of the solutions in time-coordinate (Gottlieb and Shu, 1998). On the other hand, the local monotonicity in the axial coordinate is guaranteed by the corresponding flux-limiting function (Javeed et al., 2011a; Koren, 1993). Several challenging case studies of single and multi-component elution are considered to study the effects of axial and radial dispersions on fixed-bed chromatography.

The novelty of this article specifically includes: (a) numerical approximation of nonlinear 2D-LKM using the HR-FVS of Koren, (b) injection of specific profiles to amplify the effect of possible rate limitations of the mass transfer in the radial direction, (c) validation of the accuracy and efficiency of proposed numerical scheme through comparison of its results and of other flux-limiting schemes (Javeed et al., 2011a; Leer, 1977). The developed numerical algorithm and results are seen as helpful tools for further developments of nonlinear chromatographic processes. For instance, the results could be used to study the effects of mass transfer kinetics and axial and radial dispersion coefficients on the elution profiles. The studied 2D-model and numerical schemes are more general and flexible than the classical 1D-models and numerical schemes (Javeed et al., 2011a). Further, we have provided useful numerical tools to approximate and apply this model, if required. The latter means if radial dispersion is rate limiting.

The paper is organized as follows. In Section 2, the 2D-LKM is introduced. In Section 3, the proposed HR-FVS is derived. In Section 4, different case studies are considered. Finally, conclusions are drawn in Section 5.

2. The nonlinear 2D-LKM

In the case of multi-component nonlinear 2D-LKM, the mass balances for concentrations in the liquid phase are coupled with the kinetic equations for solid phase concentrations. The model assumes that the kinetics of adsorption-desorption are infinitely fast but the mass transfer kinetics are not. The injected solute travels along the column axis in the z-direction by advection and axial dispersion, while spreads in the r-direction by radial dispersion, see Fig. 1. In this study, the flow rate variations are neglected and the interstitial velocity u is kept constant. To trigger and amplify the effect of possible rate limitations of the mass transfer in the radial
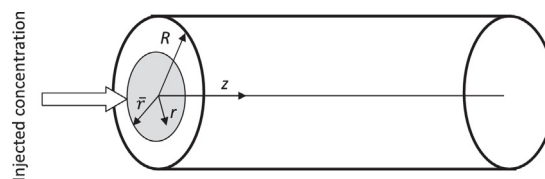

Fig. 1. Schematic diagram of a chromatographic column of cylindrical geometry.

direction, the following specific injection conditions are assumed. By introducing a parameter $\bar{r}$ the inlet cross section of the column is divided into an inner cylindrical core and an outer annular ring (c.f. Fig. 1). The injection profile is formulated in a general way allowing for injection either through an inner core, an outer ring or through the whole cross section. The latter case results if $\bar{r}$ is set equal to the radius of the column denoted by R.

Under these assumptions, the mass balance equations for concentrations of mixture components in the liquid phase can be expressed as:

$$\frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial z} = D_{z,i} \frac{\partial^2 c_i}{\partial z^2} + \frac{D_{r,i}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) - \frac{k_i}{\epsilon}(q_i^* - q_i),$$

$$\text{for} \quad i = 1, 2, \ldots, N_c. \tag{1}$$

The corresponding mass balances for mixture components concentrations in the stationary phase can be expressed as:

$$\frac{\partial q_i}{\partial t} = \frac{k_i}{1 - \epsilon}(q_i^* - q_i). \tag{2}$$

In the above equations $c_i(t, z, r)$ and $q_i(t, z, r)$ denote the ith component solute concentrations in the liquid and solid phases, respectively and q_i^* is the solid phase concentration in equilibrium of the ith component. Moreover, $D_{z,i}$ and $D_{r,i}$ represent the longitudinal and radial dispersion coefficients of the ith component, k_i is the mass transfer coefficient for the ith component, $\epsilon \in (0, 1)$ is the external porosity, and N_c denotes the number of mixture components. In addition, t, z and r denote the time, axial and radial coordinates, respectively. For sufficiently large values of k_i, for $i = 1, 2, \ldots, N_c$, the solution of multi-component 2D-LKM converges to that of multi-component 2D equilibrium dispersive model (2D-EDM).

For modeling and simulation in preparative chromatography, experimentally determined adsorption equilibrium data has to be represented by suitable mathematical equations. Different relations of isotherms are available in the literature (Guiochon et al., 2006; Ruthven, 1984). Here, we consider the generalized nonlinear Langmuir isotherm

$$q_i = \frac{a_i c_i}{1 + \sum_{j=1}^{N_c} p_j b_j c_j}, \quad i = 1, 2, 3, \ldots, N_c, \tag{3}$$

where a_i represents the Henry's coefficient of ith component, b_i quantifies the nonlinearity of the isotherm, and the terms p_j in the denominator can have positive or negative signs to allows switching between Langmuir and anti-Langmuir behaviors of the mixture components. In practice, each component in the mixture is Langmuir-like if the corresponding term in the denominator has a positive sign and is anti-Langmuir in the opposite case (Mazzotti, 2006, 2009). To simply the notations and reduce the number of variables appearing in the model equations, the following dimensionless quantities are introduced:

$$x = \frac{z}{L}, \quad \tau = \frac{ut}{L}, \quad \rho = \frac{r}{R}, \quad Pe_{z,i} = \frac{Lu}{D_{z,i}}, \quad Pe_{r,i} = \frac{R^2 u}{D_{r,i}L}, \quad \kappa_i = \frac{k_i L}{u}, \tag{4}$$