



Theoretical analysis of the influence of forced and inherent temperature fluctuations in an adiabatic chromatographic column



Shamsul Qamar^{a,b,*}, Fouzia Abdul Sattar^b, Iqra Batool^b, Andreas Seidel-Morgenstern^a

^a Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany

^b Department of Mathematics, COMSATS Institute of Information Technology, Islamabad, Pakistan

HIGHLIGHTS

- Temperature fluctuations are analyzed in an adiabatic chromatographic column.
- Analytical solutions and moments of concentration and temperature fronts are given.
- Coupling of concentration and temperature profiles is illustrated through case studies.
- Effects of essential kinetic and thermodynamic parameters are analyzed.
- The moment solutions derived are seen valuable to estimate model parameters.

ARTICLE INFO

Article history:

Received 7 September 2016

Received in revised form 22 November 2016

Accepted 13 December 2016

Available online 21 December 2016

Keywords:

Non-isothermal chromatography

Linearized isotherm

Analytical solutions

Moment analysis

Numerical solutions

ABSTRACT

A linearized non-isothermal equilibrium dispersive model (EDM) of liquid chromatography is investigated to quantify unavoidable thermal effects in adiabatic chromatographic columns. The considered model contains convection-diffusion partial differential equations (PDEs) for mass and energy balances in the mobile phase coupled with an algebraic equation for adsorption isotherm. The solution process successively employ Laplace transformation and linear transformation steps to uncouple the governing set of coupled differential equations. The resulting uncoupled systems of ordinary differential equations are solved using an elementary solution technique. The solutions are very useful to understand the speeds and shapes of concentration and thermal fronts in chromatographic columns. The moment generating property of the Laplace domain solutions is utilized to derive analytical temporal moments of the concentration and temperature profiles. These moments are seen as useful to estimate unknown model parameters from measured profiles. For illustration several case studies of practical interest are provided. To evaluate the range of applicability of analytical solutions, selected results are compared with numerical results applying a high resolution finite volume scheme considering nonlinear isotherms.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Chromatography is one of the most versatile separation techniques used for identification and purification of multi-component mixtures in many industries. It has a wide range industrial applications either as a preparative or analytical method. This technology is highly effective for the separation of complex mixtures and very similar target molecules at reasonable production and high purity levels, for instance to isolate enantiomers and to purify proteins, see Ruthven (1984), Guiochon (2002), Guiochon and Lin (2003), and Guiochon et al. (2006).

Separation of mixture components through liquid chromatography is based on their different distribution between two non-miscible phases. The first one is a stationary solid phase which is fixed in the column. The second one is a mobile liquid phase streaming through the chromatographic system. Firstly, the liquid mixture (mobile phase) is fed into a column containing a stationary phase. The stationary phase adsorbs the mixture components in varying degrees. During the migration of mixture components through the column, composition fronts develop and propagate governed by the adsorption isotherm providing a characteristics retention behavior of the species involved. Separated peaks of desired purity can be collected periodically at the outlet of the column. Being an exothermic process, adsorption is always accompanied by heat transfer, which in certain situations becomes very important.

* Corresponding author at: Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany.

E-mail address: qamar@mpi-magdeburg.mpg.de (S. Qamar).

Thermal effects are usually neglected in the liquid chromatography by assuming that the effect of heats of adsorption is negligible. For that reason, adsorption chromatography processes have often been assumed isothermal. The first analysis of thermal effects in a pulse chromatography experiment has been done by Cerro and Smith (1969). In that article, heat effects were analyzed by studying a deviation from linear chromatography through injection pulse size and concentration variations. In order to answer the question of whether the linearity of such systems is a sufficient condition to insure the absence of thermal effects, Haynes (1986) made a study based on temporal moment analysis. Zhong and Meunier (1994) have studied the interference for non-isothermal non-equilibrium perturbation chromatography by means of temporal moment analysis. They derived analytical expressions of the first and second chromatographic moments. There are few more contributions considering non-isothermal conditions in packed fixed-beds, see e.g. Sainio (2005, 2007, 2011), Vu and Seidel-Morgenstern (2011), and Qamar Javeed et al. (2012). On the other hand, thermal effects have been widely discussed in the case of gas chromatography using solid packings, see e.g. Kruglov (1994), Yongsunthorn and Alpay (1999), Xiu et al. (2002), Glöckler et al. (2006), and Eigenberger et al. (2007).

In high-pressure liquid chromatography, viscous heat generated by the friction of the eluent flowing through the packed-bed can be substantial and may cause a significant degrees rise in temperature along the column, see Gritti et al. (2016). Under steady state temperature regime, this heat generates radial temperature gradients that may cause serious losses of column efficiency, can significantly affect the solvent viscosity, and may overcome the effect of the adsorption heat. Thus, proper precautions are necessary to minimize heat losses through the column wall. For more details about this phenomenon, which is not further considered below, see the article by Gritti et al. (2016) and references therein.

Different mathematical models are available in the literature for studying chromatographic separations at the analytical and preparative scales. The most important to mention are the general rate model (GRM), the linear driving force model, the lumped kinetic model (LKM), the equilibrium dispersive model (EDM), and the ideal model, see Ruthven (1984), Guiochon (2002), Guiochon and Lin (2003), and Guiochon et al. (2006). Each model has its own level of complexity to describe the process. In this work, the non-isothermal EDM is analytically and numerically investigated. The EDM assumes that mass transfer is of infinite rate whereas the LKM incorporates the rate of variation of the local concentration of solute in the stationary phase and local deviation from equilibrium concentrations. The GRM accounts for axial dispersion and all the mass transfer resistances. The current single-component non-isothermal EDM consist of two convection-diffusion partial differential equations with dominant convective terms and coupled with an algebraic equation for isotherm.

The aim of this article is to quantify temperature gradients that occur in liquid chromatography. The joint occurrence of concentration and thermal fronts is illustrated and key parameters influencing the temperature gradients are identified. For this purpose, a linearized non-isothermal EDM is considered. The analytical solutions for concentration and energy are derived by means of Laplace transformation, see Van Genuchten (1981), Rice and Do (1995), and Javeed et al. (2013). The moment generating property of the Laplace domain solutions is utilized to get partly new analytical expressions for the temporal moments. The relevance and importance of matching theoretically and experimentally determined moments for efficient parameter estimation is known since a long time. Moment analysis approach has been comprehensively discussed in the literature, see Kubin (1965a,b), Kucera (1965), Schneider and Smith (1968), Suzuki (1973), Wolff et al. (1980.), Ruthven (1984), Lenhoff (1987), Miyabe and Guiochon (2000,

2003, 2007, 2009), Guiochon et al. (2006), Javeed et al. (2013), and Qamar and Seidel-Morgenstern (2016). Moments analysis is standard in the chromatographic community related to analyzing the second moments or the heights equivalent to a theoretical plate (HETP) as a function of flow rate in order to evaluate column efficiencies (Guiochon et al. (2006)). No systematic use is made of moments of temperature responses.

For validation of our linear assumptions, a high resolution finite volume scheme (HR-FVS) is applied to solve the model for nonlinear isotherm, see Javeed et al. (2011, 2012). Several case studies are carried out to analyze the current non-isothermal chromatographic process.

In the present research several aspects are addressed that have not been treated in this detail up to now for the considered non-isothermal EDM model. The Laplace transformation and eigen-decomposition techniques are applied to derive analytical solutions of the model equations. The temperature effects within the column are deeply discussed and analyzed. To further analyze the process, the first four temporal moments are derived for the concentration and temperature pulses. The effects of different kinetic and thermodynamic parameters are analyzed on the process. Finally, we have extended the considered HR-FVS to solve the non-isothermal model of chromatography for comparison and validation of our linear assumptions, see Javeed et al. (2011, 2012). Several test problems of practical interest are considered.

The remaining parts of the paper are organized as follows. In Section 2, the considered non-isothermal EDM is briefly introduced. In Section 3, analytical solutions of the model are derived. In Section 4, analytical temporal moments are derived from the Laplace transformed solutions. Section 5 presents the results of various case studies. Finally, conclusions are drawn in Section 6.

2. The non-isothermal equilibrium dispersive model

Consider the flow of a single-solute along with an inert carrier through a chromatographic column packed with spherical adsorbent particles. A small change in the concentration is performed by injecting a pulse of concentration into an initially equilibrated column. The following simplifying assumptions are used: (i) The column is fully initially equilibrated. (ii) The bed is homogeneous and radial concentration gradients in the column are neglected. (iii) The compressibility of the mobile phase is negligible, i.e. the fluid is incompressible. (iv) There is no interaction between the solvent (carrier) and the solid phase. (v) The packing material used in the stationary phase is made of porous spherical and uniform size particles. (vi) The equilibrium relationships are linearized. In general, adsorption equilibrium relationships are not linear, however, the linearization is realistic for small sample changes or perturbations, and can give simple characteristic results. (vii) The influence of temperature on the physical properties as viscosity, density, heat capacity, and transport coefficients as axial dispersion and axial heat conductivity can be neglected. (viii) The axial dispersion coefficient and the axial heat conductivity coefficient are assumed independent of flow rate.

The equilibrium-dispersive model (EDM) assumes that the mass transfer kinetics are of infinite rate. All contributions due to non-equilibrium and axial dispersion effects are aggregated into the corresponding apparent dispersion coefficient D_z . The classical mass balance equation of the single-component EDM for a fixed-bed chromatographic column is expressed as

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} = D_z \frac{\partial^2 c}{\partial z^2} - F \frac{\partial q^*}{\partial t}. \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/6467526>

Download Persian Version:

<https://daneshyari.com/article/6467526>

[Daneshyari.com](https://daneshyari.com)