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Breakthrough curves and elution profiles of single solutes in case of adsorption isotherms with two inflection points

Weibing Zhang[a,b], Yichu Shan[a], Andreas Seidel-Morgenstern[a,c,*]

[a] *Max-Planck-Institut für Dynamik komplexer technischer Systeme, Sandtorstrasse 1, D-39106 Magdeburg, Germany*
[b] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116011, China*
[c] *Otto-von-Guericke-Universität.für Verfahrenstechnik, Universitätsplatz 2, D-39106 Magdeburg, Germany*

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Abstract

The shape of breakthrough curves and elution profiles depends strongly on the course of the specific equilibrium functions characterizing the chromatographic system. For a highly efficient system the equilibrium theory provides a methodology how to predict the band profiles. The concept is frequently applied to analyze single component systems characterized by isotherms possessing simple shapes (Langmuir or anti-Langmuir behaviour). However, adsorption isotherms often possess more complicated shapes and have inflection points in their courses. This leads to the development of composite concentration waves and results in complex shapes of breakthrough curves and elution profiles. In this paper, the equilibrium theory is used to predict breakthrough curves for a chromatographic system characterized by an adsorption isotherm with two inflection points. The results obtained are validated by comparing with numerical solutions of the equilibrium dispersive model.

Keywords: Equilibrium theory; Adsorption isotherms; Inflection points; Breakthrough curves

1. Introduction

There are several models available which are capable to predict elution profiles for chromatographic processes under overloaded conditions [1,2]. In general these models take into account the distribution equilibria and, in different detail, mass transfer resistances. Typically the corresponding balance equations must be solved numerically. Instructive analytical solutions can be derived using the equilibrium theory of chromatography which neglects all mass transfer limitations [3–5]. These solutions describe essential features of the development of concentration profiles in chromatographic columns.

In order to apply the equilibrium theory to describe chromatographic processes the underlying distribution equilibrium functions must be provided. Under diluted conditions these functions are linear and migration speeds do not depend on concentration. If larger sample sizes are introduced in a chromatographic column the nonlinear range of the equilibrium functions becomes important and migration speeds depend on concentration. This leads to the formation of compressed and dispersed fronts. The migration speeds and the shapes of the corresponding fronts can be predicted using the equilibrium theory exploiting the method of characteristics [3–9]. The application of the concept is in particular simple and capable to predict the development of the band profile for a single component characterized by an isotherm which is completely convex or concave. Applying elegant coordinate transformations also analytical solutions were derived which describe the behavior of mixtures obeying certain types of competitive adsorption isotherms [3–5]. The powerful concept was further already extended successfully in order to predict the performance of more sophisticated multicolumn arrangements, as e.g. applied in the simulated moving bed process [10,11].

First results regarding the relation between the courses of the isotherms and the shapes of single component elution profiles were reported in [12] for equilibria of the Langmuir or anti-Langmuir type. Later Klamer and Van Krevelen [13] pointed out

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* Corresponding author. Tel.: +49 391 67 18643; fax: +49 391 67 12028.
E-mail address: andreas.seidel-morgenstern@vst.uni-magdeburg.de
(A. Seidel-Morgenstern).

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that adsorption isotherms often possess inflection points. They investigated the chromatographic behavior of a solute characterized by an isotherm with a single inflection point and they briefly illustrated already the complex profiles in case of an adsorption isotherm with two inflection points. Instructive schematic illustrations regarding the impact of inflection points in the course of an adsorption isotherms on the shape of band profiles were provided in [5,6] applying equilibrium theory. However, still there is a lack in explicit demonstrations of this relation using concrete parameters of an isotherm model and a specific chromatographic system.

In this paper, selected aspects of the equilibrium theory will be shortly revised. For illustration simple isotherms (of the Langmuir and anti-Langmuir type) will be used. Then examples of more complex isotherm shapes will be given. An experimental result will be presented to demonstrate the strong correlation between isotherm course and shape of breakthrough curves. In the main part of the paper the equilibrium theory will be applied in order to analyze step responses for a chromatographic system characterized by an adsorption isotherm possessing two inflection points. Finally, results of numerical simulations applying the equilibrium dispersive model will be presented in order to validate the analytical results obtained.

2. Relation between curvatures of adsorption isotherms and shapes of adsorption and desorption fronts

The basis of the equilibrium theory of chromatography is to neglect all kinetic effects causing band broadening and to assume that the distribution equilibrium of a solute between the mobile and stationary phases is permanently established. Thus, the following mass balance equation holds true [1–5]:

$$\frac{\partial c}{\partial t} + F\frac{\partial q(c)}{\partial t} + u\frac{\partial c}{\partial x} = 0 \tag{1}$$

In the above, c and q are the concentrations in the mobile and stationary phases and F is the phase ratio for which holds $F = (1-\varepsilon)/\varepsilon$ with ε being the total column porosity. In Eq. (1) the mobile phase velocity u is assumed to be constant as it is typically the case in liquid chromatography.

The solution of Eq. (1) requires the specification of initial and boundary conditions. Typically is assumed a fixed-bed uniformly preloaded with an initial concentration c^{Init} and a rectangular injection profile introduced between $t = 0$ and $t = t^{\text{inj}}$:

$$c(t=0,\ x) = c^{\text{Init}} \tag{2}$$

$$c(t, x=0) = \begin{cases} c^{\text{inj}} & \text{for} \quad 0 < t \le t^{\text{inj}} \\ c^{\text{Init}} & \text{for} \quad t^{\text{inj}} < t \end{cases} \tag{3}$$

If the injection time t^{inj} is large enough the whole fixed-bed is completely transformed from the first equilibrium state corresponding to the initial condition (c^{Init}, $q(c^{\text{Init}})$) into a new equilibrium state corresponding to the injection concentration (c^{inj}, $q(c^{\text{inj}})$). This problem is the classical and extensively studied Riemann problem [5]. Exploiting the method of characteristics there is a complete theory available providing the solution of Eq. (1) and discussing its properties [3–5]. The shape of the resulting breakthrough curves depends (a) on the direction of the process (adsorption for $c^{\text{Init}} < c^{\text{inj}}$, desorption for $c^{\text{Init}} > c^{\text{inj}}$) and (b) on the shape of the isotherm.

In case of nonlinear isotherms compressed fronts (shocks) or dispersed front (waves) propagate through the fixed-bed with characteristic velocities. Hereby the velocity of a shock is related to the isotherm chord between the two limiting concentrations before (c^-) and after (c^+) the shock according to:

$$u_{\text{shock}}(c^-, c^+) = \frac{u}{1 + F((q(c^+) - q(c^-))/(c^+ - c^-))} \tag{4}$$

The velocity in a simple wave depends on concentration according to:

$$u_{\text{wave}}(c^*) = \frac{u}{1 + F\,(\mathrm{d}q(c)/\mathrm{d}c)|_{c^*}} \tag{5}$$

Eqs. (1)–(5) have been studied intensively for different simple adsorption isotherm models (e.g. [1–11]). Fig. 1 illustrates for Langmuir and anti-Langmuir systems the close relation between the curvature of the isotherm and the shape of adsorption and desorption fronts. Hereby an important and general rule is the fact that operating lines for an adsorption step ($c^{\text{inj}} > c^{\text{Init}}$) or a desorption step ($c^{\text{inj}} < c^{\text{Init}}$) are given by the closest connection between these two concentrations below or above the isotherm. These two operating lines form in mathematical terms the *convex hull* of the isotherm. Thus, the operating lines follow either the slope of the equilibrium function or the chords between two characteristic concentrations. The operating lines can be considered as rubber bands connecting c^{Init} and c^{inj} on both sides of the isotherm [6,14]). Fig. 1 illustrates the well-known fact that for Langmuir the adsorption front systems is sharp whereas the desorption front is disperse. The opposite holds true for anti-Langmuir systems.

3. Isotherms with inflection points and example for corresponding breakthrough curves

Several studies devoted to classify the possible shapes of single component adsorption isotherms have been performed (e.g. [15,16]). Fig. 2 presents the classification of typical adsorption isotherms of dissolved substances given by Giles et al. [16].

Experimental results demonstrating the effect of the isotherm shape on the course of breakthrough curves were given e.g. in [17]. Fig. 3 shows breakthrough curves measured at 20 °C for the (+)-enantiomer of Tröger’s base with ethanol as the mobile phase and microcrystalline cellulosetriacetate as the stationary phase. The adsorption isotherm is characterized initially by an anti-Langmuir behavior which turns after an inflection point into Langmuir behavior (case I in Fig. 2). As a consequence step responses between $c^{\text{Init}} = 0$ and a feed concentration below the inflection point lead to a dispersed adsorption front and a sharpened desorption front. The opposite holds true if the exchange is performed above the isotherm inflection point as can be seen from the results of the second stages of the staircase experiment. The small initial increase in the detector signal is due to an impurity in the feed solution. Information regarding the range of retention times and more details including a suitable isotherm model is given in [17].