Study of the peak variance in isocratic and gradient liquid chromatography using the transport model

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ABSTRACT

The expressions accounting for the peak variance in isocratic and gradient liquid chromatography is derived from the transport model. In mathematical treatments, the dwelling time is taken into account, and the type of solvent strength, gradient profile and the variation of plate height (H) with mobile phase composition (φ) is not specified. By applying a coordinate transformation, the transport model is solved by using the Laplace transform approach. A plate height equation that is suited for both isocratic and gradient elution is obtained. Based on this equation, the plate height equations for any combination of stepwise and linear gradients are derived. These equations will be algebraic when the solvent strength is linear and the H–φ plot is parabolic. The plate height equations for single stepwise, single linear and the ladder-like gradients are also given.

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1. Introduction

Gradient liquid chromatography (GLC) can considerably enhance the separation and peak detection capabilities [1–4]. In practice it is usually implemented by changing mobile phase composition (φ) with time (t). The partition coefficient (K), which accounts for the distribution of the solute between mobile and stationary phase, is connected with φ. In many reversed phase systems, the relationship between the retention factor ($k = F_T K$, F_T denoting phase ratio) and φ can be accounted for by the linear solvent strength (LSS) model [5–8],

$$\ln k = \ln k_0 - S\varphi \tag{1}$$

where k_0 is the retention factor of the solute in 100% of the starting (weak) solvent, and S is the solvent strength parameter. Non-LSS (i.e. curving plots of $\ln k$ vs φ) has also been found in many cases especially in ion exchange chromatography [9–11]. In gradient elution, the variation of φ with t will make k (or K) a function of t. This makes the situations in gradient elution much more complicated than those in isocratic elution.

Mathematical models developed by using the mass balance approach are available to account for the band profiles obtained in chromatography. These models consist of a set of partial differential equations (PDEs), describing the mass balance of the solute in a slice of column and its kinetics of mass transfer in the column [12]. The expressions for retention time and plate height can be derived from these models. For isocratic elution, van Deemter has proposed a famous plate height equation (see Eq. (38) in Ref. [13]),

$$H = \frac{2D}{u} + \frac{2u}{k_f k}\left(\frac{k}{1+k}\right)^2 \tag{2}$$

which is derived from the analytical solution of the solid film linear driving force (SFLD) model [14],

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial Z} + F_T\frac{\partial q}{\partial t} = D\frac{\partial^2 C}{\partial Z^2} \tag{3}$$

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$$\frac{\partial q}{\partial t} = k_f(q^* - q) = k_f(KC - q) \tag{4}$$

In the above equations, H is the height equivalent to a theoretical plate (HETP), u is the linear flow velocity, C and q are the concentration of the solute in mobile and stationary phase, respectively, q^* is the stationary phase concentration in equilibrium (i.e. $q^* = KC$), Z is the axial distance starting from the column inlet, D is the axial dispersion coefficient, and k_f is the rate coefficient accounting for the contributions of the fluid-to-particle mass transfer, the intraparticle diffusion, and the sorption kinetics to band broadening [15].

The SFLD model can be further reduced to the equilibrium dispersive (ED) and the transport model [15–18]. The ED model assumes that the equilibrium of the solute between stationary and mobile phase is infinitely fast. In this model, all the mass transfer resistances are lumped into an apparent axial dispersion coefficient D_a,

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial Z} + F_T\frac{\partial q}{\partial t} = D_a\frac{\partial^2 C}{\partial Z^2} \tag{5}$$

$$q = KC \tag{6}$$

The plate height equation obtained from the ED model is [15,19],

$$H = \frac{2D_a}{u} \tag{7}$$

which is the same as the first term on the right hand side (RHS) of Eq. (2) except that D is replaced by D_a.

By contrast, the transport model neglects axial dispersion, and all the mass transfer resistances are lumped into a lumped mass transfer coefficient k_{fL} [15,17],

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial Z} + F_T\frac{\partial q}{\partial t} = 0 \tag{8}$$

$$\frac{\partial q}{\partial t} = k_{fL}(q^* - q) = k_{fL}(KC - q) \tag{9}$$

The plate height equation obtained from the transport model is

$$H = \frac{2u}{k_{fL}k}\left(\frac{k}{1+k}\right)^2 \tag{10}$$

which is the same as the second term on the RHS of Eq. (2) except that k_f is replaced by k_{fL}. Generally, Eq. (10) can be taken equivalent to Eq. (7). Miyabe and Guiochon have utilized this equivalence to calculate the value of k_{fL} from that of D_a which is derived from the breakthrough curve [15].

For gradient elution, the studies on the peak variance are usually based on the work of Poppe [20]. That work uses the ED model and makes the following assumptions:

(1) The gradient profile is not distorted by dispersion or by uptake of solvent components by the stationary phase.
(2) The column efficiency is independent of the mobile phase composition.
(3) The retention factor of the solute inside its band varies linearly with the distance from the band center.
(4) The LSS model applies to the retention of the solute studied (recently Gritti and Guiochon has pointed out that this assumption is necessary for the hold of the above assumption (3) [21,22]).
(5) The dwelling time, which accounts for the mobile phase migrating from the mixer to the beginning of the column, is neglected (note that Eqs. (14) and (26) in Ref. [20] are actually derived by ignoring the dwelling time [23,24]).

It should also be noted that the above assumptions are not always true in practice. For example, the plate height will vary with mobile phase composition and thus the assumption (2) has its limitation. Poppe et al. have also realized it. They did not include this effect in their treatment, because they thought that it would lead to unacceptable mathematical complexity [20]. Also, there is no general agreement between theoretical predictions and the experimental values of peak compression. Better models are still needed [22,25]. By using the Non-LSS model accounting for the retention and taking into account the adsorption of mobile phase component such as acetonitrile onto the stationary phase, Gritti and Guiochon have extended the Poppe's approach to the prediction of the peak compression factor in linear gradient elution [22,26].

So far, there are few studies on the application of the transport model in GLC. From Eqs. (2), (7) and (10), it can be believed that the studies on the features of the transport model in GLC may also provide some significant physical insight into the process of gradient elution. In this paper, we discuss in detail the mathematical treatments for the transport model in GLC. The expressions obtained in this work will be used in a following paper to account for the experimental data obtained in gradient elution. In the mathematical treatments, we take the dwelling time into account, and do not specify the type of solvent strength, gradient profile and the variation of H with φ. Therefore, the expressions obtained in this work may have a wide scope of application. It is also interesting to find out that there are some simple results obtained from the transport model. For example, the expressions obtained for any combination of stepwise and linear gradients are algebraic when the solvent strength is linear and the H–φ plot is parabolic.

2. Theoretical models

2.1. Assumptions for the modeling

In this work we make the following assumptions: