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Review

The van Deemter equation: Assumptions, limits, and adjustment to modern high performance liquid chromatography

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ABSTRACT

The fundamental assumptions of the van Deemter height equivalent to a theoretical plate (HETP) equation were formulated nearly 60 years ago in its rigorous final mathematical derivation in 1956. The limit of applicability of this classical theory of band broadening in chromatographic columns is discussed on the basis of accurate measurements of diffusion coefficients (in the bulk, in particles, and in column beds), of peak moments in both RPLC and HILIC, on the recent numerical solution of the Navier–Stokes equation and on the results of the simulation of the advection–diffusion transport in the bulk region of computer-generated random packed beds. A result of this discussion is that serious errors are made in the interpretations of the mass transfer mechanism in HILIC and RPLC that are based on the use of the original van Deemter expressions of the longitudinal diffusion coefficient through packed bed, of the mass transfer resistance in the mobile phase, and of the mass transfer resistance in the stationary phase. These errors are discussed and quantitatively assessed. Physically acceptable and relevant expressions are proposed to account for the true mass transfer mechanism in packed columns.

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1. Introduction

Many models of mass transfer kinetics have been developed since the early 1920s to predict the kinetic performance of gas, liquid, and supercritical chromatographic columns. The polar nature of the packing materials used early and the poor quality of the chromatograms obtained explain why the eldest models focused on accounting for the influence of adsorption and/or reaction kinetics [1–4] on the profiles predicted by the ideal model [5,6]. Later models elaborated in the 1950s included also the contribution of axial dispersion along the column [7,8]. In 1952, the landmark paper of Lapidus and Admundson provided a mathematical solution of the general mass balance equation of chromatographic columns, including axial dispersion and a first order adsorption–desorption kinetics between the mobile and the stationary phase [9]. In 1956, van Deemter, Zuiderweg and Klinkenberg used the exact mathematical solution of Lapidus and Admundson and derived a considerably simplified equation that is the exact solution in the limit case when the column efficiency is significant and the eluted band profiles narrow. Progress in the selection of packing materials rapidly made this case to become the general one. Cited yearly 15–40 times ever since, for a total of more than 1150 times, the van Deemter HETP equation is the best known chromatographic equation [10]. It provides the variation of the column height equivalent to a theoretical plate (HETP) with the linear mobile phase velocity.

In this work, Van Deemter et al. showed the mathematical equivalence between the HETP theory of Martin and Singe [11] (a discrete approach in which the column is segmented into a series of sections, the plates, of the same height in which the concentrations are considered as uniform) and the theory of a continuous column derived by Lapidus and Admundson (which assumes that axial dispersion in the mobile phase and a linear liquid driving force mass transfer kinetics between the mobile and the stationary phase act uniformly [9]). This equivalence is valid under two critical conditions: (1) The number of plates along the column is very large so that the asymptotic solutions of the models reduce to the convolution between a Gaussian and a rectangular functions; and (2) the profile of the injected sample tends toward the δ-Dirac function (pulse injection) so that the general solution simplifies further to a Gaussian function. As a result, the fundamental van Deemter equation depends on only two kinetic parameters, the apparent axial dispersion coefficient (D_L) and the apparent mass transfer coefficient, α, between the mobile and the stationary phases. Unfortunately, the original expression and these conditions are rarely mentioned in textbook and in most scientific papers related to the van Deemter equation.

In the 1950s, there were no HPLC instruments in the modern sense of this term, no on-line pumps, no detectors. The few quantitative data obtained with liquid chromatography columns were neither precise nor accurate and could not be used to validate, falsify, or refine this original equation. In 1955, however, under the impulsion of Eyring [12], Giddings and Keller began to work on the theories of gas and thin layer chromatography [13–15]. From then on, Giddings revisited exhaustively the dynamics of chromatography [16]. In the mean time, van Deemter had to make important assumptions regarding the expressions of the coefficients D_L (axial dispersion) and α (solid–liquid mass transfer). He looked at correlations and approximate expressions derived from chemical engineering science. The axial dispersion coefficient was then written as the sum of molecular diffusivity along a bed packed with non-porous particles (γD_I, where γ is the external obstruction factor and D_I the bulk diffusion coefficient) and eddy diffusivity ($\lambda u d_p$ where λ is a dimensionless coefficient, u the linear velocity, and d_p the particle diameter). The apparent mass transfer resistance ($1/\alpha$) was written as the sum of the resistances to mass transfers in the mobile and in the stationary phases. This eventually lead to the now well-known final form of the van Deemter equation with its three famous coefficients (longitudinal diffusion B, eddy dispersion A, and solid–liquid mass transfer resistance C). And sixty years went by, the pioneers have died, the subtle background of the assumptions made have faded away and too many fine points of the mass transfer in chromatography that had not been completely clarified then were progressively cast in concrete by generations of analysts.

Now, sixty years later, this form of the van Deemter equation still remains to be found in academic textbooks and scientific papers. This situation is mostly due to the fact that the van Deemter equation fits successfully to most sets of HETP data recorded with precise, modern HPLC instruments. Remarkably, this equation never fell into oblivion due to both its simplicity and easy assimilation by analysts and to the considerable theoretical developments made by Giddings in the 1960s of the dynamics of zone migration in chromatography [16]. Giddings tackled this kinetic problem by using the simple random walk model [17,18], the rigorous stochastic theory [19], and the generalized non-equilibrium theory [20–23]. Paradoxically, although the qualitative van Deemter equation is based on simple, approximate chemical engineering arguments, it describes HETP data very well, at least qualitatively. It is therefore important to analyze why its success has remained excellent over the last six decades and to find whether it is purely accidental or based on strong physico-chemical background.

The goal of this work is to revisit in detail the assumptions made in the derivation of the van Deemter equation and evaluate possible errors made in the interpretation of the mass transfer mechanism in HPLC columns when the three main independent parameters (A, B, and C) of the van Deemter equation are derived from sets of HETP data. Significant progress was made recently regarding the quantitative impacts of different sources of band broadening on the overall HETP of modern HPLC columns [24–26].

1 The longitudinal diffusion coefficient strongly depends on the nature of the particles in the column bed (non-porous, core–shell, and fully porous [27,28]) and on the retention mode, *e.g.* HILIC [29] or RPLC [27,28] retention mechanism. Accurate measurements of the diffusion coefficients through either the packed bed or each individual particle rely on the use of more sophisticated