Development of Correct Kinetic Plot Methods for SFC.

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Kinetic plots bring into account the relationship between plate height, column permeability, particle size and column length in one type of curve. In order to construct kinetic plots in HPLC, the plate height is measured as a function of the mobile phase velocity by varying the mobile phase velocity on a column with fixed length and this information is then extrapolated to any given column length in order to construct the kinetic plots. This is possible on the basis that $H$ and solute retention are independent of solvent compressibility issues. These approximations are valid for most HPLC applications but not for SFC separations because in SFC the retention factor ($k$) and diffusion coefficients ($D_m$) of the analytes vary with changing mobile phase velocity due to the compressible nature of the mobile phase. In this work, an experimental method to construct Van Deemter and kinetic plots is developed where the column length is not fixed but where the $k$ is kept constant as a function of flow rate by keeping the inlet and outlet pressure of the column (and thus the average pressure in the column) a constant. This method is compared to a method where the average pressure over the column is kept constant in combination with a fixed column length (isopycnic method). By comparing the resulting Van Deemter and kinetic plots with plots that are constructed using the erroneous method where $k$ is not a constant as a function of the flow rate, we can present a simple and fast way to produce correct Van Deemter and kinetic plots for SFC. This allows, for example, for the first time for a more truthful comparison between the performance of SFC and HPLC systems.