CRITICAL EVALUATION OF VARIOUS KINETIC PLOT METHODS FOR SFC SYSTEM PERFORMANCE PREDICTION AND COMPARISON WITH HPLC

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Kinetic plots have gained a lot interest in the last decade because, contrary to the Van Deemter curves, the former bring into account the relationship between plate height, column permeability, particle size and column length in one type of curve. In order to construct a Van Deemter curve and kinetic plots in HPLC, the plate height is first 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 extrapolation is possible on the basis that H and solute retention are independent of solvent compressibility issues, approximations which are valid for most HPLC applications. However, in SFC the mobile phase is compressible and thus the retention factor (k) and diffusion coefficients (D_m) of the analytes vary with changing mobile phase velocity. As a result, the measured values for H do not truly show the evolution of the performance with the mobile phase velocity, because also the other parameters that influence H (like k and D_m) are not kept constant and extrapolation errors are made when applying the conventional kinetic plot method developed for HPLC to SFC. 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. Because this fundamentally correct methodology, which is demonstrated for the first time in this work, is less practical, it is also compared to a method where only the average pressure over the column is kept constant and a fixed column length is used to measure the H values (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, also for the first time for a more truthful comparison between the performance of SFC and HPLC systems.