

A theoretical model for retention time differences

Two models have been developed to describe the change in retention time, t_R , of a solute molecule in a mobile phase, A, as function of a gradient in time of volume fraction, Φ_B , of a more- or less polar solvent, B [1]. These are (I) the displacement model, in which solute molecules are displaced at the column surface by the polar solvent molecules, B [1-3]; and (II) the model for the reversed-phase system with a polar mobile phase, A [4, 5]. In the second model, the column capacity factor k (Φ_B) > 0 for a solute molecule as a function of the volume fraction of the organic solvent, B, in the mobile phase is given by

$$k(\Phi_B) = k_a * e^{-m*\Phi_B} \quad (1)$$

where $k_a > 0$ is the capacity factor of the column for the solute molecule in pure water, A, and Φ_B the dimensionless fraction of volume of the less polar solvent ACN, which may vary between 0 and 1, and, m , a dimensionless factor > 0 . The retention time of a solute molecule is a function of a time delay after which the solute molecule experiences the gradient of Φ_B due 1) to a dwell time, τ , caused by the dead volume of tubes before the column or start of the experiment; and 2) to the position, z , of the solute molecule in the column, which varies between 0 and the length of the column, L [6]. All formula of this model are well explained [6], except for the complex reciprocal function $d[f^{-1}(\varphi_a(t^*))] / k(\varphi_a(t^*))$ in the gradient-free period, τ , applying pure water, A, as mobile phase :

$$\frac{d[f^{-1}(\varphi_a(t^*))]}{k(\varphi_a(t^*))} = \text{constant} * t^* \quad (2)$$

where time $t^* = t - (z/u) - \tau$ is the time, t , corrected for the delay or dead time τ and position, z , of the solute molecule in the column, where z varies between 0 and L , u is the speed of the mobile phase, and the quotient $L/u = t_m$ is the retention time of the mobile phase. If no gradient of ACN is applied during the LC separation, $\Phi_B = 0$, the following relation holds [6] :

$$\int_{t=0, z=0}^{t=t_{R,a}, z=L} \left\{ \frac{d[f^{-1}(\varphi_a(t^*))]}{k(\varphi_a(t^*))} \right\} = \int_{t^*=-\tau}^{t^*=t_{R,a}-t_m-\tau} \left\{ \frac{d[f^{-1}(\varphi_a(t^*))]}{k(\varphi_a(t^*))} \right\} = \text{constant} * t_{R,a} - \text{constant} * t_m = t_m \quad (3)$$

The retention time, $t_{R,a}$, of a solute molecule in pure solvent, A, is given by [3, 7]:

$$t_{R,a} = (1 + k_a) * t_m \quad (4)$$

Substitution of $t_{R,a}$ in equation (3) by (4) results in

$$\text{constant} = \frac{1}{k_a}, \text{ and consequently } \frac{d[f^{-1}(\phi_a(t^*))]}{k(\phi_a(t^*))} = \frac{t^*}{k_a} \quad (5)$$

The integral of the reciprocal function $d[f^{-1}(\phi_b(t^*))] / k(\phi_b(t^*))$ in the gradient in time period, applying a linear increasing volume fraction ϕ_b of ACN with slope $b > 0$ is:

$$\int_{t^*=0}^{t^*=t_R-t_m-\tau} \left\{ \frac{d[f^{-1}(\phi_b(t^*))]}{k(\phi_b(t^*))} \right\} = \int_{t^*=0}^{t^*=t_R-t_m-\tau} \left\{ \frac{d[\frac{\phi_b(t^*)}{b}]}{k_a * e^{-m*\phi_b(t^*)}} \right\} = \int_{t^*=0}^{t^*=t_R-t_m-\tau} \left\{ \frac{d[e^{m*b*t^*}]}{m*b*k_a} \right\} \quad (6)$$

The solution of the integrals over gradient free (5) and gradient in time period (6) is [6]

$$t_R = \frac{1}{m*b} \ln\{1 + m * b * [(k_a * t_m) - \tau]\} + t_m + \tau \quad (7)$$

It is not likely that the difference in τ – which, on the sophisticated LC system, is expected to be in seconds – is the cause of the difference in retention time between two experiments. Neither can it explain that we always observe a converging retention time, thus smaller difference in retention time between two experiments as a function of the duration of the LC run. Equation (7) is therefore simplified with $\tau = 0$

$$t_R = \frac{1}{m*b} \ln\{1 + m * b * k_a * t_m\} + t_m \quad (8)$$

The differential of equation (8) is

$$\frac{dt_R}{dk_a} = \frac{t_m}{1+m*b*k_a*t_m} \quad (9)$$

Combination of equation (8) and (9) results in

$$dt_R = dk_a * t_m * e^{-mb(t_R - t_m)} \quad (10)$$

Equation (10) explains that the difference in retention time dt_R drops nearly to zero with an increase of the slope of gradient ACN in time, b . Due to small differences in τ in s, some difference dt_R from 0 may still remain (equation 7).

References

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