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Solute Retention and Resolution in Parallel-current Open Tubular Liquid Chromatography

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Recently a new type of capillary separation was introduced by Slais et al., which they called parallel-current open-tubular liquid chromatography (PC-OTLC) [1,2]. In this mode of open tubular liquid chromatography, both the mobile phase and the pseudo-stationary phase (i.e., the retentive layer at the capillary wall) move in the same direction, however, with different velocities. The suggested method is very convenient from a practical point of view and contributes considerably to the applicability of open tubular liquid chromatography (OTLC).

Solute retention. To describe solute retention in this mode of OTLC, a mathematical model was derived, resulting in an expression for the reduced capacity factor, $k_i^*$ (Equation 24, reference 1):

$$k_i^* = \frac{\phi - q}{1 + q}$$

where $\phi$, $q$ and $K_i$ are the phase ratio, the flow ratio, and the solute distribution constant, respectively. The phase ratio is given by (Equation 22, reference 1):

$$\phi = \frac{S_r}{S_m}$$

where $S_r$ and $S_m$ are the cross-sections of the retentive phase and the mobile phase, respectively. The flow ratio is given by (Equation 10, reference 1):

$$q = \frac{F_r}{F_m}$$

where $F_r$ and $F_m$ are the flow rates of the retentive phase and the mobile phase, respectively. In this model the reduced capacity factor, $k_i^*$, is defined as in chromatography:

$$k_i^* = \frac{t_{si}}{t_0} - 1$$

where $t_{si}$ is the solute retention time and $t_0$ the migration time of an unretained compound. However, in conventional chromatographic processes there is an immobile stationary phase, whereas in this mode of OTLC the pseudo-stationary phase moves in the same direction of the mobile phase with a lower velocity. In this respect this technique has much in common with micellar electrokinetic capillary chromatography (MECC), introduced by Terabe et al. [3,4]. In MECC two phases can also be distinguished, moving in the same direction with different velocities, viz. an electroosmotically pumped aqueous phase and a micellar pseudo-stationary phase. If the solute retention in PC-OTLC is described in the same way as in MECC, the capacity factor, $k'$, is given by

$$k' = \frac{t_{si} - t_0}{t_0 \left[ 1 - \frac{t_{si}}{t_r} \right]}$$

where $t_{si}$ is the solute retention time, $t_0$ the migration time of an unretained compound and $t_r$ the migration time of a compound that is completely dissolved and carried in the retentive phase. The velocities of the solute, $v_s$, the mobile phase, $v_0$, and the retentive phase, $v_r$, can be expressed by (Equations 4 and 8, reference 1):
Combination of Equations 5, 6, 7, and 8 leads to the following equation for the capacity factor:

$$k'_i = \phi K_i$$  \hspace{1cm} (9)

where $\phi$ and $K_i$ are the phase ratio and the thermodynamic distribution constant, respectively. From Equation 9 it can be seen that defined in this way the capacity factor is independent of the flow ratio $q$. The difference between Equations 1 and 9 is illustrated in Figure 1. The solubility parameter, $\Delta s$, is defined as

$$\Delta s = s_1 - s_2$$  \hspace{1cm} (10)

where $s_1$ and $s_2$ are the solubilities of the retentive phase in the mobile phase at the inlet temperature and the capillary temperature, respectively. From Figure 1 it can be seen that at low values for $\Delta s$ only small differences between $k_i$ and $k'_i$ are observed. However, at higher values for $K_i$ and $\Delta s$ the differences become more significant and higher values for $k'_i$ are calculated. From Figure 1A it can also be seen that if $K_i$ tends to infinity, $k'_i$ tends to a finite value, given by (Equation 25, reference 1):

$$k_{i,K_i\rightarrow\infty}'^{*} = \frac{\phi}{q} - 1$$  \hspace{1cm} (11)

Resolution. If Equation 4 is used to describe the solute retention in PC-OTLC, the resolution, $R_s$, for two closely eluting peaks is given by

$$R_s = \frac{\sqrt{N} \alpha - 1}{\alpha} \frac{k_i^*}{k_i^* + 1}$$  \hspace{1cm} (12)

where $N$ and $\alpha$ are the number of theoretical plates and the selectivity, respectively. From Equation 12 it can be concluded that the resolution increases if $k_i$ increases and that the optimum resolution is obtained if $k_i$ tends to its maximum value (i.e., if $K_i$ tends to infinity). If, however, Equation 5 is used to describe the solute retention in PC-OTLC, the following equation for the resolution can be derived:

$$R_s = \frac{\sqrt{N} \alpha - 1}{\alpha} \frac{k_i^*}{k_i^* + 1} \frac{1 - t_0}{t_r + k_i^*}$$  \hspace{1cm} (13)
The last term in Equation 13 indicates the influence of the moving pseudo-stationary phase. The parameter $t_0/t_r$ is the elution window and is given by

$$
t_0/t_r = \frac{v_r}{v_0} = \frac{F_r S_m}{S_r F_m} = \frac{\phi q}{\phi}
$$

(14)

The function $f(k'_i)$ is given by

$$
f(k'_i) = \frac{k'_i}{k'_i + 1} \frac{1 - t_0/t_r}{1 + t_0/k'_i}
$$

(15)

In Figure 2 calculated graphs are shown of $f(k'_i)$ versus $k'_i$ for different values of the solubility parameter, $\Delta s$ (v/v) of (a) 0.1, (b) 0.01, (c) 0.001, and (d) 0.0001, and for $t_0/t_r = 0$ (dashed line).

Figure 2. Dependence of the resolution factor, $f(k'_i)$ on the capacity factor, $k'_i$, with $t = \eta_r/\eta_m = 10$ and values for the solubility parameter, $\Delta s$ (v/v) of (a) 0.1, (b) 0.01, (c) 0.001, and (d) 0.0001, and for $t_0/t_r = 0$ (dashed line).

The optimum capacity factor, $k'_i^{\text{opt}}$, at which the maximum resolution is obtained can be calculated by differentiating Equation 15:

$$
k'_i^{\text{opt}} = \frac{t_r}{t_0} = \frac{\phi}{\sqrt{q}}
$$

(16)

These values are lower than the corresponding values of $k'_i^*$, calculated with Equation 11, in all cases.

If Equations 5 and 9 are used to describe the solute retention in PC-OTLC, the same strategy as in MECC can be applied for resolution optimization [5,6]. Moreover, differences in the flow ratio caused by inhomogeneity of the retentive film will lead to differences in $k'_i^*$, whereas the calculated values of $k'_i$ will be unaffected because $k'_i$ is independent of the flow ratio, $q$. For these reasons we believe that Equations 5 and 9 are to be preferred to describe the solute retention in PC-OTLC.

References

Authors’ Response
When we compare the equations published in the comments of Prof. Cramers [1] and ours [2], we can say that there is no contradiction in any case. Prof. Cramers’ proposal of the description of the solute retention in terms of $k'$, which is based on the MECC concept, could be convenient in some cases, but the analogy with MECC is only formal. In such a concept, the knowledge of the migration time of the compound completely dissolved in the retention phase, $t_0$, is needed. However, it is not easily accessible in the single PC-OTLC experiment. Our estimations based on Figure 3 [2] indicate that $t_0$ is more than one order of magnitude higher than the elution time of an unretained compound, $t_r$, in the practically interesting cases. It is substantially more than in typical MECC. In our experiment [2], $\phi = 0.229$ and $q = 0.00705$; then $t_0/t_r = 32.5$. Therefore, the elution window is substantially greater than it is in MECC. At the same time, the $t_0/t_r$ term in Equations 13
and $15 \ [1]$ is small in comparison with unity ($t_0/t_r = 0.0308$ from above values) and thus, the influence of $t_r$ on the resolution, $R_s$, can be expected to be only small in the practically interesting cases. Therefore, the formal description of solute retention in PC-OTLC closer to that of conventional LC might also be acceptable.

References