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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 Šlais 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 is usual 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

$$k' = \frac{t_{si}}{t_0} - 1$$

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):

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Figure 1. Dependence of the two different defined capacity factors, (A) \( k'^*_i \) and (B) \( k'^*_i \), on the thermodynamic distribution constant, \( K_i \), with \( t = \eta_s/\eta_m = 10 \), and values for the solubility parameter, \( \Delta s (\nu/\nu) \) of (a) 0.1, (b) 0.01, (c) 0.001, and (d) 0.0001.

\[
\nu_s = \frac{F_m + F_r K_i}{S_m + S_r K_i} \quad (6)
\]
\[
\nu_0 = \frac{F_m}{S_m} \quad (7)
\]
\[
\nu_r = \frac{F_r}{S_r} \quad (8)
\]

Combination of Equations 5, 6, 7, and 8 leads to the following equation for the capacity factor:

\[
k'^*_i = \phi K_i \quad (9)
\]

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

\[
\Delta s = s_1 - s_2 \quad (10)
\]

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):

\[
k_{i, K_i \to \infty}^* = \frac{\phi}{q} - 1 \quad (11)
\]

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

\[
R_s = \frac{\sqrt{N}}{4} \frac{\alpha - 1}{\alpha} \frac{k_i^*}{k_i^* + 1} \quad (12)
\]

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:

\[
R_s = \frac{\sqrt{N}}{4} \frac{\alpha - 1}{\alpha} \frac{k_i'}{k_i' + 1} \frac{1 - \frac{t_0}{t_r}}{1 + \frac{t_0}{t_r} k_i'} \quad (13)
\]
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

\[
t_0 = \frac{v_r}{v_0} = \frac{F_r S_m}{S_r F_m} = \frac{q}{\phi}
\]  

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

\[
f(k'_i) = \frac{k'_i}{k'_i + 1} \left( 1 + \frac{t_0}{t_r} \right) - \frac{t_0}{t_r}
\]  

In Figure 2 calculated graphs are shown of \( f(k'_i) \) versus \( k'_i \) for different values of the solubility parameter, \( \Delta s \). The value zero for the elution window is the elution time of an immobile stationary phase. In this case the last term of Equation 15 becomes unity and Equation 13 equals Equation 12. In Figure 2 the maximum values for \( k'_i \), calculated with Equation 11, and the function \( f(k'_i) \) for this situation are shown (dashed line). As can be seen from Figure 2, the function \( f(k'_i) \) decreases if \( \Delta s \) increases, \( i.e. \), if the parameter \( t_0/t_r \) increases.

The optimum capacity factor, \( k'_{opt} \), at which the maximum resolution is obtained can be calculated by differentiating Equation 15:

\[
k'_{opt} = \frac{t_r}{t_0} = \frac{\phi}{q}
\]

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 \( t_r/t_0 = 32.5 \). 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 14 needs to be considered as a non-negligible factor in the resolution calculation. In this way, the resolution optimization in PC-OTLC can be performed by adjusting the flow ratio and the other parameters as in MECC.
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