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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):

$$k_i^* = \frac{\phi - q}{\frac{1}{K_i} + q} \quad (1)$$

where ϕ , 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):

$$\phi = \frac{S_r}{S_m} \quad (2)$$

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):

$$q = \frac{F_r}{F_m} \quad (3)$$

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:

$$k_i^* = \frac{t_{si}}{t_0} - 1 \quad (4)$$

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

$$k'_i = \frac{t_{si} - t_0}{t_0 \left[1 - \frac{t_{si}}{t_r} \right]} \quad (5)$$

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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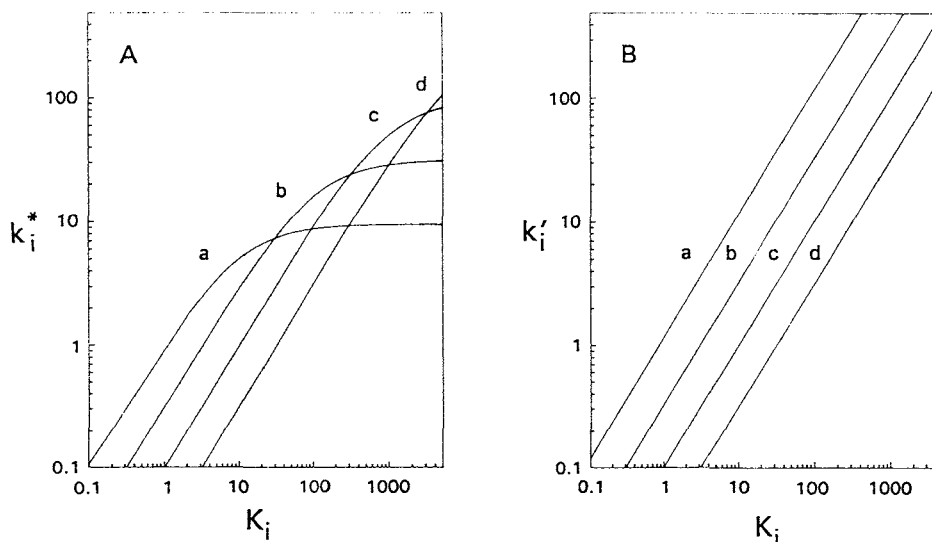


Figure 1. Dependence of the two different defined capacity factors, (A) k_i^* and (B) k_i' , on the thermodynamic distribution constant, K_i , with $t = \eta_r/\eta_m = 10$, and values for the solubility parameter, Δs (v/v) of (a) 0.1, (b) 0.01, (c) 0.001, and (d) 0.0001.

$$v_s = \frac{F_m + F_r K_i}{S_m + S_r K_i} \quad (6)$$

$$v_0 = \frac{F_m}{S_m} \quad (7)$$

$$v_r = \frac{F_r}{S_r} \quad (8)$$

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 ϕ 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, Δs , 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 Δs only small differences between k_i^* and k_i' are

observed. However, at higher values for K_i and Δs 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):

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

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 α 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:

$$R_s = \frac{\sqrt{N}}{4} \frac{\alpha - 1}{\alpha} \frac{k'_i}{k'_i + 1} \frac{1 - \frac{t_0}{t_r}}{1 + \frac{t_0}{t_r} k'_i} \quad (13)$$

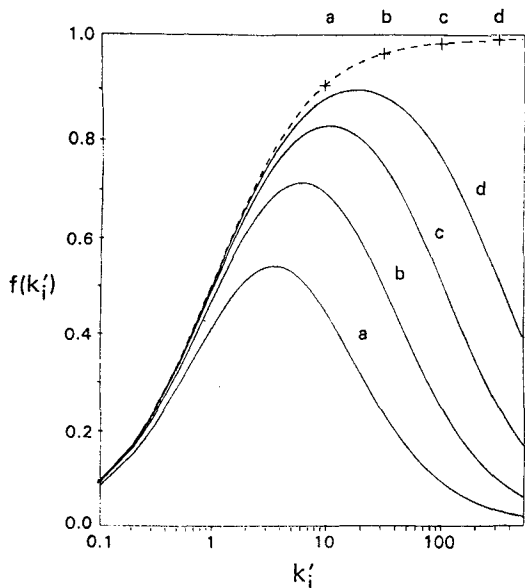


Figure 2. Dependence of the resolution factor, $f(k'_i)$ on the capacity factor, k'_i , with $t = \eta_r/\eta_m = 10$ and values for the solubility parameter, Δs (v/v) of (a) 0.1, (b) 0.01, (c) 0.001, and (d) 0.0001, and for $t_0/t_r = 0$ (dashed line).

The 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

$$\frac{t_0}{t_r} = \frac{v_r}{v_0} = \frac{F_r S_m}{S_r F_m} = \frac{q}{\phi} \quad (14)$$

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

$$f(k'_i) = \frac{k'_i}{k'_i + 1} \frac{1 - \frac{t_0}{t_r}}{1 + \frac{t_0}{t_r} k'_i} \quad (15)$$

In Figure 2 calculated graphs are shown of $f(k'_i)$ versus k'_i for different values of the solubility parameter, Δs . The value zero for the elution window t_0/t_r corresponds to 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 Δs 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:

$$k'_{opt} = \sqrt{\frac{t_r}{t_0}} = \sqrt{\frac{\phi}{q}} \quad (16)$$

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

1. K. Šlais, M. Horká, and K. Klepárník, *J. Chromatogr.* **605**, 167 (1992).
2. K. Šlais, M. Horká, *J. Microcol. Sep.* **5**, 63 (1993).
3. S. Terabe, K. Otsuka, K. Ichikawa, A. Tsuchiya, T. Ando, *Anal. Chem.* **56**, 113 (1984).
4. S. Terabe, K. Otsuka, T. Ando, *Anal. Chem.* **57**, 834 (1985).
5. J.P. Foley, *Anal. Chem.* **62**, 1302 (1990).
6. J. Vindevogel and P. Sandra, *Introduction to Micellar Elektrokinetic Chromatography* (Hüthig Buch Verlag, Heidelberg, 1992).

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_r , is needed. However, it is not easily accessible in the single PC-OTLC experiment. Our estimations based on Figure 3 [2] indicate that t_r is more than one order of magnitude higher than the elution time of an unretained compound, t_0 , 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 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

1. P.G.H.M. Muijselaar and C.A. Cramers, *J. Microcol. Sep.* **5**, 187 (1993).
2. K. Šlais, M. Horká, and K. Klepárník, *J. Chromatogr.* **605**, 167 (1992).