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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  $\phi$ ,  $q$  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):

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

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:

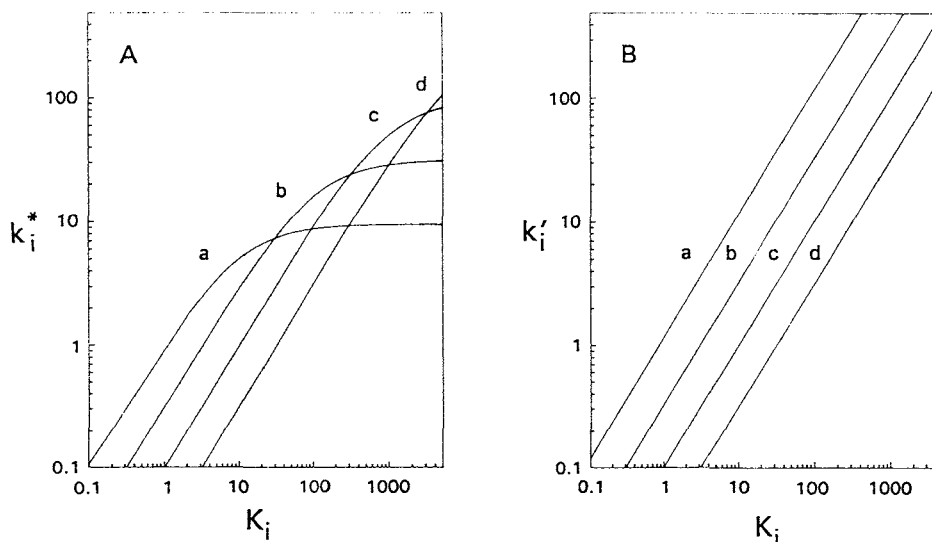
$$k_i^* = \frac{t_{si}}{t_0} - 1 \quad (4)$$

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,  $\Delta s$  ( $v/v$ ) 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  $\phi$  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):

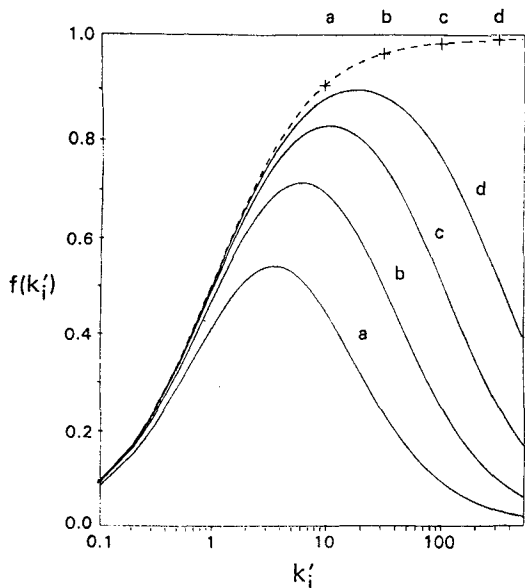
$$k_{i,K_i \rightarrow \infty}^* = \frac{\phi}{q} - 1 \quad (11)$$

**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  $\alpha$  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:

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



**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 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,  $\Delta s$ . 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  $\Delta s$  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:

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

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.

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### 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.

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