

NOTE

Optimization of Capillary Zone Electrophoresis and Micellar Electrokinetic Capillary Chromatography

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Optimization of capillary zone electrophoresis based on an electrosmotic mobility of ions. A new optimum condition relating electrophoretic mobility of ions and electroosmotic mobility was obtained using new resolution equation proposed in previous work incorporating effective length. Optimization of micellar electrokinetic capillary chromatography was done on the new resolution equation proposed in previous work based on incorporating effective length. This optimization for micellar electrokinetic capillary chromatography was done for resolution and t_R/R_s^2 which t_R is retention time and R_s is the resolution.

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In our work¹ a new model based on effective length migrated on a similar to tread mill case for capillary zone electrophoresis (CZE) was constructed. New resolution and number of theoretical plates for capillary zone electrophoresis were proposed.

Similar treatment was applied to micellar electrokinetic capillary chromatography (MECC) and new equations obtained for the number of theoretical plates and resolution equations for various cases of operation².

It is interesting to observe, what are the optimum conditions for capillary zone electrophoresis and micellar electrokinetic capillary choromatography under operation. In the present work optimum conditions for the operation of both capillary zone electrophoresis and micellar electrokinetic capillary choromatography

have been found based upon new resolution equations obtained in previous works^{1,2} for these two techniques of separation.

Optimization of capillary zone electrophoresis: For capillary zone electrophoresis the two fundamental equations are migration time equation given by Jorgenson and Lukacs³:

$$\mathbf{t}_{s} = \left(\frac{\mathbf{L}^{2}}{\boldsymbol{\mu}_{eo} + (\boldsymbol{\mu}_{ep})_{AB}}\right) \mathbf{V}$$
(1)

And resolution equation given by previous work¹:

$$R = \left(\frac{FV}{32RT} (\mu_{ep})_{AB}\right)^{1/2} \left(\frac{(\mu_{ep})_A - (\mu_{ep})_B}{\mu_{ep} + (\mu_{ep})_{AB}}\right)^{3/2}$$
(2)

We optimize the resolution with respect to $(\mu_{ep})_{AB}$. The characteristic function for the resolution to optimize is:

$$f(\mu_{ep})_{AB} = \frac{(\mu_{ep})_{AB}^{1/2}}{[\mu_{eo} + (\mu_{ep})_{AB}]^{3/2}}$$
(3)

$$\frac{\mathrm{d}f(\mu_{\mathrm{ep}})_{\mathrm{AB}}}{\mathrm{d}(\mu_{\mathrm{ep}})_{\mathrm{AB}}} = 0 \tag{4}$$

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$$\frac{df(\mu_{cp})_{AB}}{d(\mu_{cp})_{AB}} = \frac{1/2(\mu_{cp})_{AB}^{-1/2}[\mu_{co} + (\mu_{cp})_{AB}]^{3/2} - 3/2[\mu_{co} + (\mu_{cp})_{AB}]^{1/2}(\mu_{cp})_{AB}^{1/2}]}{[\mu_{co} + (\mu_{cp})_{AB}]^{3}} = 0$$
 (5)

This equation has fortunately an analytical answer. The condition that eqn. 5 is maintained with some simple algebraic manipulation is going to be:

$$\mu_{eo} = 9^{1/3} \mu_{ep}^{2/3} - \mu_{ep} \tag{6}$$

Therefore if eo and ep meet the condition of (eqn. 6) the optimum resolution occurs.

For further curiosity the condition (eqn. 6) is plotted in Fig. 1. It is shown that in the beginning μ_{eo} increases with μ_{ep} reaches a maximum and then decreases. For all these points on this curve there are going to be maximums occur for the resolution.

Optimization for micellar electrokinetic capillary chromatography: In a previous work⁴ we did optimization for micellar electrokinetic capillary choromatography but that work the resolution equation uses Terabe's resolution equation⁵



which dose not contain effective length. In present work the new resolution equation² is used for optimization.

The two fundamental equations one for retention time⁵ and one for the resolution equation included effective length² are shown:

$$\mathbf{t}_{\mathrm{R}} = \left(\frac{1+\mathbf{k}'}{1+\left(\frac{\mathbf{t}_{0}}{\mathbf{t}_{\mathrm{mc}}}\right)\mathbf{k}'}\right)\mathbf{t}_{0}$$
(7)

$$R_{s} = \frac{1}{4} \left(\frac{(D_{ep})_{B} RT}{F} \right)^{1/2} N_{pseudo}^{1/2} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k'}{k' + 1} \right)^{3/2} \left(\frac{1 - (t_{0} / t_{mc})}{1 + (t_{0} / t_{mc})k'} \right) (8)$$

The characteristic equation needed to be optimized is:

$$f(k') = \left(\frac{k'}{k'+1}\right)^{3/2} \left(\frac{1 - (t_0 / t_{mc})}{1 + (t_0 / t_{mc})k'}\right)$$
(9)

Fortunately eqn. 10 has an analytical answer. That answer is:

$$k' = \frac{\frac{t_{0}}{t_{mc}} + \sqrt{\left(\frac{t_{0}}{t_{mc}}\right)^{2} + 24\left(\frac{t_{0}}{t_{mc}}\right)}}{4\left(\frac{t_{0}}{t_{mc}}\right)}$$
(11)

Table-1 shows optimum k' which makes resolution optimum, for t_0/t_{mc} that are typically between 0.1 to 0.5. k' for this range is between 4.13 to 2. This range of k' is typical for the column chromatography⁴.

TABLE-1									
t_0/t_{mc}	0.1	0.2	0.3	0.4	0.5				
k'	4.13	3.00	2.50	2.20	2.00				

This reasonable range is another evidence for supporting the incorporation of effective length for the new resolution equation².

Karger *et al.*⁶ obtained the optimum capacity factor for t_R/R_s^2 . This optimization shows the optimum capacity factor which makes the retention time minimum as well. If we obtain t_R/R^2 the characteristic equation is:

$$f(\mathbf{k}') = \frac{\frac{1+\mathbf{k}'}{1+\left(\frac{t_0}{t_{mc}}\right)\mathbf{k}'}}{\left(\frac{\mathbf{k}'}{\mathbf{k}'+1}\right)^3 \left[\left(\frac{1-\left(\frac{t_0}{t_{mc}}\right)}{1+\left(\frac{t_0}{t_{mc}}\right)\mathbf{k}'}\right)\right]^2}$$
(12)

$$\frac{\mathrm{d}\mathbf{f}(\mathbf{k}')}{\mathrm{d}\mathbf{k}'} = 0 \tag{13}$$

Equation 13 has an analytical solution:

$$k = \frac{3\left(\frac{t_0}{t_{mc}}\right) + \sqrt{9\left(\frac{t_0}{t_{mc}}\right)^2 + 24\left(\frac{t_0}{t_{mc}}\right)}}{4\left(\frac{t_0}{t_{mc}}\right)}$$

Table-2 shows that optimum range of k' which makes t_R/R_s^2 maximum, for t_0/t_{mc} that are typically between 0.1 to 0.5. k' for this is between 4.69 to 2.63. This range of k' is typical for column chromatography too⁶.

TABLE-2									
t_0/t_{mc}	0.1	0.2	0.3	0.4	0.5				
k'	4.69	4.42	3.11	2.83	2.63				

Conclusion

The optimum condition was obtained for capillary zone electrophoresis. It is interesting that the optimum k' for the resolution and t_R/R_s^2 is in the some range for micellar electrokinetic capillary choromatography. It is also interesting that the derivative equations have fraction of power but fortunately they have very nice analytical answers.

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