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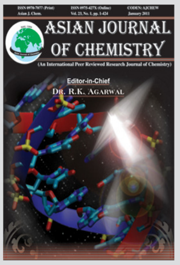

Correction to the Resolution Equation for Micellar Electrokinetic Capillary Chromatography for Various Cases

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A new model based on effective length migrated on a similar to tread mill case for various modes of operation in capillary zone electrophores was constructed. In present work similar treatment has been applied to micellar electrokinetic capillary chromatography and new equations obtained for the number of theoretical plates and resolution equations.

Key Words: Capillary zone electrophoresis, Micellar electrokinetic capillary, Choromatography, Resolution equation.

INTRODUCTION

Terabe *et al.*[1] proposed micellar electrokinetic capillary chromatography and by a treatment similar to chromatography by defining pseudo capacity factors for the micelle which are considered as stationary phase and the aqueous phase as the mobile phase.

Since micelles are not realy stationary, we defined new term effective mobility of neutral solute and new equation for migration time and resolution equations obtained for neutral solute in terms of effective mobility for neutral solute[2].

In present work there is a need to construct a model for micellar electrokinetic capillary chromatography based on defining effective length for the neutral analyte which travels under the presence of electric field and with the micelle. Neutral analyte intracts with the micelle due to their hydrophobicity and micelle intracts with the electric field due to its charge.This new model for micellar electrokinetic capillary chromatography is constructed based on tread mill case and it is similar to previous work which was done for capillary zone electrophoresis[3].

Micellar electrokinetic capillary chromatography

We defined effective mobility for the neutral solute[2]. The effective electrophoretic mobility of the neutral solute can be defined as[2].

$$(\mu^{*}_{ep})_{AB} = \left[\frac{(n_{mc})_{AB}}{(n_{aq})_{AB} + (n_{mc})_{AB}}\right]\mu_{ep} \qquad (1)$$

$$(n_{mc})_{AB} = \frac{1}{2}\left[(n_{mc})_A + (n_{mc})_B\right] \qquad (2)$$

$$(n_{aq})_{AB} = \frac{1}{2}\left[(n_{aq})_A + (n_{aq})_B\right] \qquad (3)$$

$$(\mu^{*}_{ep})_{AB} = \frac{1}{2}\left[(\mu^{*}_{mc})_A + (\mu^{*}_{ep})_B\right] \qquad (4)$$

where n_{mc} and n_{aq} are the total moles of the solutes in the micelle and aqueous phase, respectively and μ_{ep} is the electrophoretic mobility of the micelle. By the use of capacity factor definition $k' = \frac{(n_{mc})_{AB}}{(n_{aq})_{AB}}$ the effective electrophoretic mobility can be shown in terms of capacity factor and electrophoretic mobility of the micelle[2].

$$(\mu^{*}_{ep})_{AB} = \left(\frac{k'}{1+k'}\right)\mu_{ep} \qquad (5)$$

We define the other mobility, the effective migration mobility of the solute, μ_s^* as the summstion of the effective electrophoretic mobility of the solute and electroomotic mobility.

$$(\mu^{*}_{s})_{AB} = (\mu^{*}_{ep})_{AB} + \mu_{eo} \qquad (6)$$

The resolution R_s was defined in previous work is given as[3]:

$$R_s = \left[\frac{(t_R)_B - (t_R)_A}{(t_R)_{AB}}\right]\frac{\sqrt{N}}{4} \qquad (7)$$

By insertion of $t_s = \frac{L}{\mu_s E}$ in eqn. 7 where L is the length of capillary and E is the electric field between the two ends of the capillary and some algebraic manipulation, we obtain:

$$R_s = \left[\frac{(\mu_s^*)_A - (\mu_s^*)_B}{(\mu_s^*)_{AB}}\right]\frac{\sqrt{N}}{4} \tag{8}$$

where $$(\mu_s^*)_{AB} = \frac{(\mu_s^*)_A - (\mu_s^*)_B}{2} \tag{9}$$

μ_s^* given by eqn. 6 is substituted in eqn. 8 from which we derive expression:

$$R_s = \left[\frac{(\mu_{ep}^*)_A - (\mu_{ep}^*)_B}{\mu_{eo} + (\mu_{ep})_{Ab}}\right]\frac{\sqrt{N}}{4} \tag{10}$$

N, number of theoretical plates is equal to $\frac{L'}{H}$. L′ is the effective length that solute travels, similar to discussion we had for effective length in capillary zone electrophores, but unfortunately not only in the work of Terable *et al.*[1,4] but also in our work[2], L is treated as the length of capillary, similar to conventional column chromatography which number of theoretical plates is difined as $N = \frac{L}{H}$. In our work[2] we discussed three cases for micellar electrokinetic capillary chromatography in terms of μ_{mc} the net micelle mobility. Which is defined as:

$$\mu_{mc} = \mu_{eo} + \mu_{ep} \tag{11}$$

Where μ_{ep} is the electrophoretic mobility of the micelle and μ_{eo} is the electroosmotic mobility.

Before we introduce the three cases we have assumed that mobility is positive if its direction is the same as the electroosmotic flow vector and it is negative if its direction is opposite to electroosmotic flow.The electric field in this relation $\nu = \mu E$ is considered the magnitude of a vector.

Case I[2]

Case I occurs when $\mu_{mc} \prec 0$ and $\mu_{ep} + \mu_{eo} \prec 0$ and $-\mu_{ep} \succ \mu_{eo}$ for this case[2] which has been referred to by Terabe *et al.*[5] as negative $\frac{t_o}{t_{mc}}$ the micelles migrate in a direction opposite to the electroosmotic flow. However, for separation the solute should migrate in the same direction as the electroosmotic flow. In order to maintain this condition, the effective migration mobility of the solute, μ_s^* must be greater than zero.

$$(\mu_s^*)_{AB} = (\mu_{ep}^*)_{AB} + \mu_{eo} \succ 0 \tag{12}$$

Similar to the discussion we had for capillary zone electrophores[3] where the effective length for this case, of micellar electrokinetic capillary chromatography is

$$(\upsilon_{ep}^*)_{AB}\, t = L' \text{ where } (\upsilon_{ep}^*)_{AB} = (\mu_{ep}^*)_{AB} E$$

Accoding to Terabe *et al.*[4,5] there are five causes of band broadening and the overall column plated height is given as:

$$H = H_L + H_{mc} + H_{aq} + H_t + H_{ep} \tag{13}$$

We organized theoretical plate height as[2]:

$$H_L = \frac{(B_m' + B_s')L}{\mu_{eo} V} \tag{14}$$

$$H_s = C_s' \mu_{eo} \frac{V}{L} \tag{15}$$

$$H_m = C_m' \mu_{eo} \frac{V}{L} \tag{16}$$

Setting $H_t = 0$[4] and the electrophoretic dispersion contribution to the plate height (H_{ep}) has been obtaind[4]:

$$H_{ep} = E' \mu_{eo} \frac{V}{L} \tag{17}$$

$$N = \frac{L'}{H_L + H_{mc} + H_{aq} + H_{ep}} \tag{18}$$

$$L = t(\mu_s^*)_B E \tag{19}$$

$$L = t[\mu_{eo} + (\mu_{ep}^*)_B]E \tag{20}$$

$$t = \frac{L}{[\mu_{eo} + (\mu_{ep}^*)_B]E} \tag{21}$$

where $-(\mu_{ep})_B \prec \mu_{eo}$

Substituting (eqn. 21) into $L' = t(\mu^*_{ep})_B$ and then substituting for L′ from eqn. 18 one gets:

$$N = \frac{(\mu_{ep}^*)_B L}{[\mu_{eo} + (\mu_{ep}^*)_B][H_l + H_{mc} + H_{aq} + H_{ep}]} \tag{22}$$

Substituting from (eqn. 14) to (eqn. 17) into (eqn. 22) N is obtained to be:

$$N = \frac{(\mu_{ep}^*)_B L^2 \mu_{eo} V}{[\mu_{eo} + (\mu_{ep}^*)_B][(B_m' + B_s')L^2 + (C_s' + C_m' + E')\mu_{eo}^2 V]} \tag{23}$$

where $-(\mu_{ep}^*)_B \prec \mu_{eo}$

Then substituting (eqn. 23) into resolution (eqn. 10) R_s is obtained to be

$$R_s = \left[\frac{(\mu_{ep}^*)_A - (\mu_{ep}^*)_B}{\mu_{eo} + (\mu_{ep}^*)_{AB}}\right]\frac{1}{4} \left[\frac{(\mu_{ep}^*)_B L^2 \mu_{eo} V}{[\mu_{eo} + (\mu_{ep}^*)_B][(B_m' + B_s')L^2 + (C_s' + C_m' + E')\mu_{eo}^2 V^2]}\right]^{\frac{1}{2}} \tag{24}$$

where $-(\mu_{ep})_B \prec \mu_{eo}$

By referring to definitions of B'_s, C'_s, C'_m and E'[3]

We see that they all have the term $\left[1 + \left(\frac{t_0}{t_{mc}}\right)k'\right]$ in the denominators, then

$$B_0^{\prime\prime} = B_0^{\prime}\left[1+\left(\frac{t_0}{t_{mc}}\right)k'\right] \qquad (25)$$

$$B_m^{\prime\prime} = B_m^{\prime}\left[1+\left(\frac{t_0}{t_{mc}}\right)k'\right] \qquad (26)$$

$$B_s^{\prime\prime} = B_s^{\prime}\left[1+\left(\frac{t_0}{t_{mc}}\right)k'\right] \qquad (27)$$

$$C_s^{\prime\prime} = C_s^{\prime}\left[1+\left(\frac{t_0}{t_{mc}}\right)k'\right] \qquad (28)$$

$$C_m^{\prime\prime} = C_m^{\prime}\left[1+\left(\frac{t_0}{t_{mc}}\right)k'\right] \qquad (29)$$

$$E'' = E'\left[1+\left(\frac{t_0}{t_{mc}}\right)k'\right] \qquad (30)$$

$\left(\frac{t_0}{t_{mc}}\right)=\left(\frac{\mu_{mc}}{\mu_{eo}}\right)$ and substituting eqns. 25, 28, 30 into eqn. 24, eqn. 31 is obtained for the resolution.

$$R_s = \frac{(\mu_{ep}^{*})_A - (\mu_{ep}^{*})_B}{[\mu_{eo} + (\mu_{ep}^{*})_{AB}]}\cdot(\mu_{ep}^{*})_B^{½}\left(\frac{1}{4}\right)\left[\frac{(k'+1)L^2V}{B''^2+(C_s^{\prime\prime}+C_m^{\prime\prime}+E'')\mu_{eo}^2V^2}\right]^{\frac{1}{2}} \qquad (31)$$

Resolution is thus expressed as a function of basic electrochemical parameters. R_s can also be transformed to its chromatography from by multiplying the numerator and the denominator of eqn. 31 by $(k' + 1)^{½}$ and setting $\frac{k_B^{\prime}}{k_A^{\prime}} = \alpha, k_A^{\prime} = k'$ and $\mu_{ep} = \mu_{mc} - \mu_{eo}$, we obtain this intermediate expression:

$$R_s = \frac{1}{4}\left[\frac{\alpha-1}{\alpha}\right]\left[\frac{k_B^{\prime}}{1+k_B^{\prime}}\right]\left[\frac{1-\mu_{mc}/\mu_{eo}}{1+(\mu_{mc}/\mu_{eo})k_B^{\prime}}\right](\mu_{ep}^{*})_B^{½}\cdot\left[\frac{\mu_{eo}L^2V}{(B_m^{\prime\prime}+B_s^{\prime\prime})L^2+(C_s^{\prime\prime}+C_m^{\prime\prime}+E'')\mu_{eo}^2V^2}\right]^{\frac{1}{2}} \qquad (32)$$

Eqn. 32 can be transformed further to yield the chromatography form by substituting

$$\left(\frac{\mu_{mc}}{\mu_{eo}}\right)=\left(\frac{-t_0}{t_{mc}}\right) \text{ and } \nu_{eo} = \mu_{eo}\frac{V}{L}$$

and making some algebraic manipulation

$$R_s = \frac{1}{4}\left[\frac{\alpha-1}{\alpha}\right]\left[\frac{k_B^{\prime}}{1+k_B^{\prime}}\right]\left[\frac{1-t_0/t_{mc}}{1-(t_0/t_{mc})k_B^{\prime}}\right](\mu_{ep}^{*})_B^{½}\cdot\left[\frac{L}{(B_m^{\prime\prime}+B_s^{\prime\prime})/\nu_{eo}+(C_s^{\prime\prime}+C_m^{\prime\prime}+E'')\nu_{eo}}\right]^{\frac{1}{2}} \qquad (33)$$

Since N is not L/H for micellar electrokinetic capillary chromatography the last term in above equation is not N but in order to compare above equation with column chromatography we call L/H pseudo, N_{pesudo} = L/H and we substitute

$$(\mu_{ep}^{*})_B = \left[\frac{k_B^{\prime}}{(1+k_B^{\prime})}\right]\mu_{ep} \qquad (34)$$

$$\frac{D}{\mu} = \frac{RT}{F}, (\mu_{ep})_B = \frac{F}{RT}(D_{ep})_B \qquad (35)$$

By substituting eqns. 25 to 30, and 34 and 35 into eqn. 33, R_s is produced as:

$$R_s = \frac{1}{4}\left(\frac{(D_{ep})_B RT}{F}\right)^{\frac{1}{2}}\left[\frac{\alpha-1}{\alpha}\right]\left[\frac{k_B^{\prime}}{1+k_B^{\prime}}\right]^{\frac{3}{2}}\left[\frac{1+(t_0/t_{mc})}{1-(t_0/t_{mc})k_B^{\prime}}\right]N_{pseudo}^{½} \qquad (36)$$

The resolution eqations given by Terabe *et al.*[1] and Ghowsi's equation for the resolution eqn. 36 for micellar electrokinetic capillary chromatography are given below:

$$R_s = \frac{N^{½}}{4}\cdot\frac{\alpha-1}{\alpha}\cdot\frac{k_B^{\prime}}{1+k_B^{\prime}}\cdot\frac{1+(t_0/t_{mc})}{1-(t_0/t_{mc})k_B^{\prime}} \qquad (37)$$

By comparing eqn. 36 with column chromatography equation for resolution[6], expression $\left[\frac{1+(t_0/t_{mc})}{1-(t_0/t_{mc})k_B^{\prime}}\right]$ has been added which has been mentioned by Terabe[1]. As shown in eqn. 37 in Terabe's resolution equation $\frac{k_B^{\prime}}{k_B^{\prime}+1}$ is replaced by $\left[\frac{k_B^{\prime}}{k_B^{\prime}+1}\right]^{\frac{3}{2}}$

The expression in selectivity factor is the same for both Terabe and Ghowsi's resolution equations.

$$R_s = \frac{1}{4}\left(\frac{(D_{ep})_B RT}{F}\right)^{\frac{1}{2}}\cdot N_{pseudo}^{½}\cdot\left[\frac{\alpha-1}{\alpha}\right]\cdot\left[\frac{k_B^{\prime}}{k_B^{\prime}+1}\right]^{\frac{3}{2}}\left[\frac{1+(t_0/t_{mc})}{1-(t_0/t_{mc})k_B^{\prime}}\right] \qquad (38)$$

$\left[(D_{ep})_B\frac{RT}{4F}\right]^{\frac{1}{2}}$ is a new term in Ghowsi's equation (eqn. 38) which relates the fundamental equation of resolution to the effective diffusion of solute B.

Case II[2]

$\mu_{eo} = -\mu_{ep}$ or $\mu_{mc} = 0$. In this case, the micelle is stationary and the net velocity is zero. This case is equivalent to

$$\frac{t_{mc}}{t_0} = \frac{\mu_{eo}}{\mu_{mc}} \text{ or } \frac{t_0}{t_m} = \frac{\mu_{mc}}{\mu_{eo}} = 0$$

Now the chromatographic situation pertains and by using eqns. 32 and 33, and substituting $\frac{\mu_{mc}}{\mu_{eo}} = 0$ or $\frac{t_0}{t_{mc}} = 0$ one obtains.

$$R_s = \frac{1}{4}\left[\frac{\alpha-1}{\alpha}\right]\left[\frac{k'_B}{1+k'_B}\right](\mu^*_{ep})^{½}_B \cdot$$

$$\left[\frac{\mu_{eo} L^2 V}{(B'_m + B'_s L^2) + L^2 (C'_s + C'_m + E')\mu_{eo}^2 V^2}\right]^{\frac{1}{2}} \tag{39}$$

$$R_s = \frac{1}{4}\left[\frac{\alpha-1}{\alpha}\right]\left[\frac{k'_B}{1+k'_B}\right](\mu^*_{ep})^{½}_B \cdot$$

$$\left[\frac{L}{((B'_m + B'_s)/\nu_{eo}) + (C'_s + C'_m + E')\nu_{eo}}\right]^{\frac{1}{2}} \tag{40}$$

Using B'_m, B'_s, C'_s, C'_m and E' given in the appendix of reference[2]. The should be simplified because $\frac{t_0}{t_{mc}} = 0$

$$B'_m = \frac{D_{aq}}{k'_B} \tag{41}$$

$$B'_s = 2k'_B D_{mc} \tag{42}$$

$$C'_s = \frac{2k'_B}{1+k'_B} \cdot \frac{\nu_{eo}}{k_d} \tag{43}$$

$$C''_m = \left(\frac{k'_B}{1+k'_B}\right) \cdot \frac{d^2 \nu_{eo}}{4D_{aq}} \tag{44}$$

$$E' = 0.026 k'_B \cdot \frac{\nu_{eo}}{k_d} \tag{45}$$

Substituting eqns. 41 to 45 into eqn. 40 one obtains:

$$R_s = \frac{1}{4}\left[\frac{\alpha-1}{\alpha}\right]\left[\frac{k'_B}{1+k'_B}\right](\mu^*_{ep})^{½}_B \cdot$$

$$\left[\frac{L}{\frac{(D_{aq}/k'_B + 2k'_B D_{mc})}{\nu_{eo}} + \frac{2k'_B}{1+k'_B} \cdot \frac{\nu_{eo}}{k_d} + \left(\frac{k'^2_B}{1+k'_B}\right)\frac{d^2\nu_{eo}}{4D_{aq} + 0.026k'_B}\frac{\nu_{eo}}{k_d}}\right]^{½}$$

Case III[2]

$\mu_{mc} \succ 0$ or $-\mu_{ep} \prec \mu_{eo}$. This mode is the conventional mode of operation for micellar electrokinetic capillary chromatography. Since the assumptions are similar to assumptions for **case I**. The only difference is that micelle moves in the same direction as electroosmotic flow. The resolution equation is similar to eqn. 36, the only difference is that the term

$$\frac{1+\left(\frac{t_0}{t_{mc}}\right)}{1-\left(\frac{t_0}{t_{mc}}\right)k'_B} \text{ is replaced by } \frac{1-\left(\frac{t_0}{t_{mc}}\right)}{1+\left(\frac{t_0}{t_{mc}}\right)k'_B}$$

Conclusion

The resolution equation obtained by Terabe[1] is transformed into the equation with electrochemical parameters.The effective length which was not incorporated into the resolution equation[2] was performed. The resolution equation obtained for micellar electrokinetic capillary chromatography in terms of electrochemical parameters were transformed back into chromatographic one. The results between obtained resolution equation Ghowsi's equation and Terabe's work are given in eqns. 37 and 38.

List of symbols

N:	Number of theoretical plates; separation efficiency
R:	Gas constant
T:	Temperature
F:	Faraday constant
V:	Potential across capillary
E:	Electric field
X:	Length of capillary
t:	Migration time
ν_{eo}:	Electroosmotic velocity
ν_{ep}:	Electrophoretic velocity
$(\nu_{ep})_{AB}$:	Average migration time for species A and species B
μ_{eo}:	Electroosmatic mobility
$(\mu_{ep})_{AB}$:	Average electrophoretic mobility for species A and specics B
D:	Diffusion constant
μ_{ep}:	Electrophoretic mobility of the micelle
$(\mu_{ep})_A$:	Electrophoretic mobility of species A
$(\mu_{ep})_B$:	Electrophoretic mobility of species B
f:	Force
X':	Effective length traveled by the species under electric force f
H:	Theoretical plate height
R_s:	Resolution
(n_{mc}):	Concentration of solute in micellar phase
(n_{aq}):	Concentration of solute in aqueous phase
$(n_{mc})_{AB}$:	Average concentration of solute A and solute B in micellar phase
$(n_{aq})_{AB}$:	Average concentration of solute A andsolute B in aqueous phase
$(\mu^*_{ep})_{AB}$:	Average effective mobility of neutral solute A and neutral solute B
k':	Capacity factor

μ^*_s:	Effective migration mobility of solute
$(\mu^*_s)_{AB}$:	Average effective migration mobility of solute A and solute B
$(\mu^*_s)_A$:	Effective migration mobility of solute A
$(\mu^*_s)_B$:	Effective migration mobility of solute B
(ν^*_{ep}):	Effective velocity of neutral solute
H_L:	Longtitutenal dispersion plate height
H_{mc}:	Micellar phase dispersion plate height
H_{aq}:	Aqueous phase dispersion plates height
H_t:	Thermal dispersion plate height
H_{ep}:	Electrophoretic dispersion plate height
t_0:	Migration time for an unretainned solute
t_{mc}:	Migration time for a micelle
α:	Selectivity factor

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