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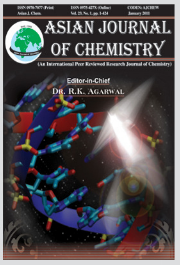

Correction to the Number of Theoretical Plates and Resolution Equation for Capillary Zone Electrophoresis and Micellar Electrokinetic Capillary Choromatography

Kiumars Ghowsi[1,*] and Hosein Ghowsi[2]

[1]Department of Chemistry, Islamic Azad University, Majlesi Branch, Isfahan, I.R. Iran
[2]Department of Mathematics, Payame Noor University, 19395-4697, Tehran, I.R. Iran

*Corresponding author: E-mail: k_ghowsi@yahoo.com

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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 has been constructed. New resolution and number of theoretical plates for capillary zone electrophoresis have been proposed. Similar treatment has been applied to micellar electrokinetic capillary chromatography and new equations obtained for the number of theoretical plates and resolution equations for various cases of operation.

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

INTRODUCTION

The origin of theoretical plates has been obtained from the work of Giddings[1]. Giddings has derived the following equation for the number of theoretical plates.

$$N = \frac{-\Delta\mu^{ext}}{2\theta RT} \quad (1)$$

where coefficient θ = unity when molecular diffusion acts alone and exceed unity when other process contributes. R = gas constant and T = temperature and μ^{ext} = chemical potential. Conventionally substitution of $\Delta\mu^{ext}$ into eqn. 1 gives for the number of theoretical plates.

$$N = \frac{ZFV}{2RT} \quad (2)$$

For an ideal process, in which θ = 1 and 298 K, this equation reduces

$$N = 20ZV \quad (3)$$

where we have used F = 96500 coulombs/mol. This, voltage drops in the range of 100-1000 V with Z capable of yielding *ca.* 2000-200000 theoretical plates, a range comparable to that found in chromatographic system. Jorgenson and Lukacs[2], also provided a theory for capillary zone electrophoresis (CZE) in which they proposed two fundamental equations for resolution and migration time. Resolution and number of theoretical plates are the focus of this work. This is how number of theoretical plates are derived for capillary zone electrophoresis and used in resolution equation by Jorgenson and Lukacs[2] by starting with Gidding s number of theoretical plates

$$N = \frac{ZFV}{2RT} \quad (4)$$

V = potential across capillary is substituted by EX where E = electric field and X = length of the capillary. Z = charge number for ion is assumed to be 1, hence

$$N = \frac{EFX}{2RT} \quad (5)$$

$$X = t[\nu_{eo} + (\nu_{ep})_{AB}] \quad (6)$$

Eqn. 6 where $(\nu_{ep})_{AB} = \frac{1}{2}[(\nu_{ep})_A + (\nu_{ep})_B)$ is substituted by X in eqn. 5.

$$N = \left[\left(\frac{E}{2RT}\right)Et[\nu_{eo} + (\nu_{ep})_{AB}\right] \quad (7)$$

There is a mistake occurs in Jorgenson and Lukacs work[2], t in eqn. 7 is replaced by eqn. 8, this is the case when electroosmosis is absent.

$$t = \frac{X}{\nu_{ep}} \quad (8)$$

By making this mistake substitution, what has been obtained by Jorgenson and Lukacs for N, eqn. 2, is

$$N = \frac{F}{2RT}E\left[\left(\frac{X}{\nu_{ep}}\right)((\nu_{eo}) + (\nu_{ep})_{AB})\right] \quad (9)$$

E, X is the, V, voltage across the capillary and ν_{ep} and ν_{ep} are substituted by μ_{ep} and $\mu_{eo}E$.

$$N = \left(\frac{FV}{2RT}\right)\frac{\mu_{eo} + (\mu_{ep})_{AB}}{(\mu_{ep})_{AB}} \tag{10}$$

By using Einstain relation eqns. 11a and 11b we substitute for μ_{ep} from enq. 11b

$$\frac{D}{\mu_{ep}} = \frac{RT}{F} \tag{11a}$$

$$\mu_{ep} = \frac{FD}{RT} \tag{11b}$$

and simplify, then eqn. 12 is obtained

$$N = \frac{V}{2D}[\mu_{eo} + (\mu_{ep})_{AB}] \tag{12}$$

D = diffusion constant. This is the equation fo the number of theoretical plates the Jorgenson and Lukacs use to obtain the resolution. N = driven by mistake[2]. The resolution R_S is given by them.

$$R_S = \frac{(\mu_{ep})_A - (\mu_{ep})_B}{\mu_{eo} + (\mu_{ep})_{AB}}\frac{\sqrt{N}}{4} \tag{13}$$

Substituting eqn. 12 for N into eqn. 13, the resolution can be expressed as

$$R_S = \frac{((\mu_{ep})_A - (\mu_{ep})_B)}{(\mu_{eo} + (\mu_{ep})_{AB})^{1/2}} \cdot \frac{\sqrt{V}}{4\sqrt{2D}} \tag{14}$$

The above eqn. 14 is the same equation that was obtained by Jorgenson and Lukacs[2].This equation is incorrect. In the present work equaton for resolution which is considered correct equation is proposed[3].

Theory

According to Gidding's theory[1] the evaluation of the ultimate capabilities of zone electrophoresis is possible. To calculate the number of theoretical plates and separable zone achieveable in ideal zone electrophoresis, the electrostatic force exerted on a mole of charged particles on electric field of strength E is

$$\text{Force} = ZFE = f \tag{15}$$

where Z = net charge of a single particle in proton units and F = Faraday constant the negative chemical potential drop across the separation path.

$$-\Delta\mu^{ext} = fx' \tag{16}$$

In which X' is the distance where f, force applied in capillary electrophoresis. For conventional mode of capillary zone electrophoresis, electroosmotic and electrophoretic velocities are in opposite direction. This conventional mode is similar to tread mill and electric stairs where the morning object has two movement one walking and the other one movement of the stairs.

There X' in eqn. 16 is not the length of capillary, it is effective distance where the electric force which is applied is greater then the length of capillary is called X'.

$$-\Delta\mu^{ext} = fx' \tag{17}$$

Then by substituting eqn. 17 into eqn. 1 the eqn. 18 for the number of theoretical plates results.

$$N = \frac{fX'}{2RT} \tag{18}$$

X' = effective lenngh which looks like a treadmill, the solute is like a person which can run for miles on the mill but actually he has stayed stationary, f = FE force is Faraday constant times electric filed. By substituting force in enq. 18 one gets.

$$N = \frac{F}{2RT}EX' \tag{19}$$

By definition, the effective distance the analyte travels under the force of electric filed, X' divided by the retention times, t, is equivalent to electrophretic $(\nu_{ep})_{AB}$ mobility is given as the following.

$$(\nu_{ep})_{AB} = \frac{X'}{t} \tag{20}$$

where $(\nu_{ep})_{AB} = \frac{1}{2}[(\nu_{ep})_A + (\nu_{ep})_B]$.

By the help of eqn. 20 X' can be substituted into eqn. 19. Now eqn. 21 can be rewritten to include electrophoretic velocity.

$$N = \left(\frac{F}{2RT}\right)(\nu_{ep})_{AB}Et \tag{21}$$

Replacing the electrophoretic velocity variable with the product of electrophoretic mobility and electric field $\nu_{ep} = \mu_{ep}E$ yields the following expression:

$$N = \left[\left(\frac{F}{2RT}\right)[(\mu_{ep})_{AB}E^2t\right] \tag{22}$$

In order to observe the dependence, efficiency has on capillary length and electroosmosis, a substitution for the time variable in eqn. 20 is made. Net displacement of the analyte or capillary length, X, is related to the retention time, t as shown

$$N = t[\nu_{eo} + (\nu_{ep})_{AB}] \tag{23}$$

Rearrangement of eqn. 23 gives eqn. 24

$$t = \frac{X}{\nu_{eo} + (\nu_{ep})_{AB}} \tag{24}$$

Substituting eqn. 24 into eqn. 19 yields the expression,

$$N = \frac{F}{2RT}\left(\frac{(\nu_{ep})_{AB}}{\nu_{eo} + (\nu_{ep})_{AB}}\right)XE \tag{25}$$

By making additional substitutions for electrophoretic and electroosmotic velocity produced, $\nu = (\mu_{ep})_{AB}$ and $\nu = \mu_{eo}E$, a final equation for efficiency is

$$N = \left(\frac{F}{2RT}\right)\left(\frac{(\mu_{ep})_{AB}}{\mu_{eo} + (\mu_{ep})_{AB}}\right)XE \tag{26}$$

Plate height is the ratio of effective length X' to efficiency N is

$$H = \frac{X'}{N} \tag{27}$$

Substituting equation into eqn. 27 yields an expression for plate height.

$$H = \frac{2RT}{FE} \tag{28}$$

This interesting result shows that the theoretical plate height is independent of electroosmotic flow when it is based on the effective distance the analyte travels rather than the capillary length. Instead, plate height has a simple inverse relation with the electric field strength.

Fig. 1 shows the inverse relation between theoretical plate height and electric field strength. Electric filed strength is the voltage across two ends of capillary divided by the length of capillary.

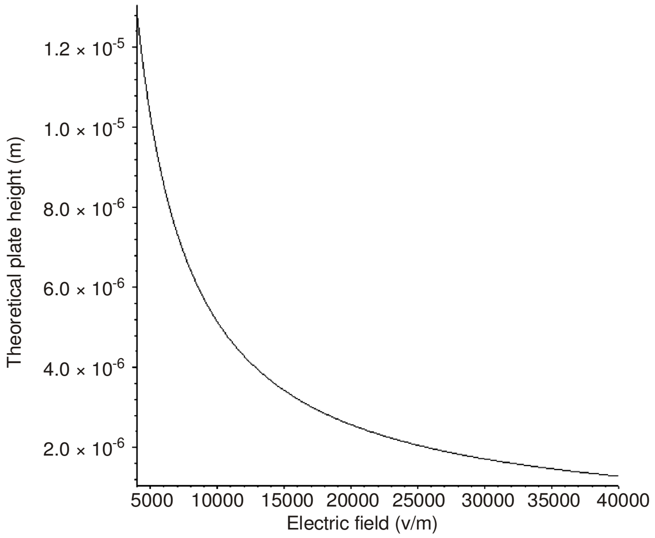

Fig. 1

Equation for resolution: Base width resolution is the quantitative measure of ability to separate two analytes. For two adjacent peaks with similar elution times, peak should be nearly identical:

$$W_A \approx W_B \approx W_{AB} \tag{29}$$

where $W_{AB} = \frac{1}{2}(W_A + W_B)$.

Assuming eqn. 29 is true, resolution for species A and B expressed in terms of their retention times and the peak base width for either species[2].

$$R_S = \frac{(t_R)_B - (t_R)_A}{W_{AB}} \tag{30}$$

The convetional expression for separation can be written with parameters related to either species A or B, shown here using the retention time and peak base width for species B[2].

$$N = 16\left[\frac{(t_R)_B}{W_{AB}}\right]^2 \tag{31}$$

By combining eqns. 30 and 31 an equation for chromatography is produced that expresses resolution in terms of efficiency and retention times[4].

$$R_S = \frac{\sqrt{N}}{4}\left[\frac{(t_R)_B - (t_R)_A}{(t_R)_{AB}}\right] \tag{32}$$

The resolution time variable t_R and the efficiency N are eliminated by inserting eqns. 24 and 25 into eqn. 32 for the analyte B:

$$R = \left[\left(\frac{F}{32RT}\right)\left(\frac{(\nu_{ep})_{AB}}{(\nu_{ep})_{AB} + \nu_{eo}}\right)XE\right]^{1/2}\left[\frac{(\nu_{ep})_A - (\nu_{ep})_B}{(\nu_{ep})_{AB} + \nu_{eo}}\right] \tag{33}$$

When electrophoretic ν_{ep} velocity, is replaced with $\mu_{ep}E$ and applied potential, V is substituted for XE one obtains the following equation for the resolution:

$$R_S = \left[\frac{FV(\mu_{ep})_{AB}}{32RT}\right]^{1/2}\left[\frac{(\mu_{ep})_A - (\mu_{ep})_B}{(\mu_{ep} + (\mu_{ep})_{AB})^{3/2}}\right] \tag{34}$$

In order to make a comparison between resolution equation derived, eqn. 34, Jorgenson Lukacs equation[2] for resolution eqn. 14 could be transformed to the following equation by

Using Einstein relation $\frac{D}{\mu} = \frac{RT}{F}$

and $$R_S = \left[\frac{FV}{32RT(\mu_{ep})_{AB}}\right]^{1/2}\left[\frac{(\mu_{ep})_A - (\mu_{ep})_B}{(\mu_{eo} + (\mu_{ep})_{AB})^{1/2}}\right] \tag{35}$$

Jorgenson and Lukacs equation (eqn. 36) and new derived Ghowsi equation (eqn. 37) for resolution are given as

$$R_S = \left[\frac{FV}{32RT(\mu_{ep})_{AB}}\right]^{1/2}\left[\frac{(\mu_{ep})_A - (\mu_{ep})_B}{(\mu_{eo}\,_{-}{+}\,(\mu_{ep})_{AB})^{1/2}}\right] \tag{36}$$

$$R_S = \left[\frac{FV(\mu_{ep})_{AB}}{32RT}\right]^{1/2}\left[\frac{(\mu_{ep})_A - (\mu_{ep})_B}{(\mu_{eo} + (\mu_{ep})_{AB})^{3/2}}\right] \tag{37}$$

This interesting observation that for the absence of electroosmotic flow in Jorgenson and Lukacs equation the resolution eqn. 35 is converted to

$$R_S = \left[\frac{FV}{32RT}\right]^{1/2}\left[\frac{(\mu_{ep})_A - (\mu_{ep})_B}{(\mu_{ep)})}\right] \tag{38}$$

The other resolution equation obtained in present work Ghowsi s eqn. 34 without presence of electroosmotic flow or $\mu_{eo} \le \mu_{ep}$ is converted to

$$R_S = \left[\frac{FV}{32RT}\right]^{1/2}\left[\frac{(\mu_{ep})_A - (\mu_{ep})_B}{(\mu_{ep})_{AB}}\right] \tag{39}$$

It is interesting that only for this case resolution equation of Jorgenson Lukacs eqn. 14 with the help of Einstein relation is equal to Ghowsi s derived equation for resolution eqn. 38 at present work for capillary zone electrophoresis.

Micellar electrokinetic capillary chromatography

By converting the figure of merits[5] in MECC to electrochemical parameters[3] and pursuing similar procedure we applied to capillary electrophoresis and using effective length solute travels rather than length of capillary and then converting the resolution equation in terms of chromatography parameters new equation for resolution could be found which is going to be published in another paper[6].

Conclusion

The fundamental eqn. 12 for the number of theoretical plates has been used to obtain resolution equation by Jorgenson eqn. 14. The number of theoretical plates equation in previous work by Jorgenson is wrong, automatically make the resolution eqation wrong. With the consideration that length X in eqn. 17 is the distance where force is applied in capillary electrophoresis, number of theoretical plates which depends on eqn. 17 is discussed. Another equation is the result obtained in eqn. 28 which indicates the new result based on effective length. In comparison with eqn. 12 Jorgenson equation diffrernt eqn. 26 has been used to obtain eqn. 34 which is the new resolution equation similar procedure could be applied to obtain the number of theoretical plates for effective length for MECC and the new resolution eqution could be obtained too. This work for MECC will be shown in a future work[6].

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