Interaction of electroosmotic flow on isotachophoretic transport of ions

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Abstract—A numerical study on the influence of electroosmotic flow on analyte preconcentration by isotachophoresis (ITP) is made. We consider that the double layer induced electroosmotic flow (EOF) counterbalance the electrophoretic velocity and a stationary ITP stacked zones results. We solve the Navier-Stokes equations coupled with the Nernst-Planck equations to determine the local convective velocity and the preconcentration dynamics of ions. Our numerical algorithm is based on a finite volume method along with a second-order upwind scheme. The present numerical algorithm can capture the sharp boundaries of step-changes (plateau mode) or zones of steep gradients (peak mode) accurately. The convection of ions due to EOF reduces the resolution of the ITP transition zones and produces a dispersion in analyte zones. The role of the electrokinetic parameters which induces dispersion is analyzed. A one-dimensional model for the area-averaged concentrations based on the Taylor-Aris type effective diffusivity is found to be in good agreement with the computed solutions.

Keywords: Interfaces, Electroosmotic flow, QUICK Scheme, Dispersion, Effective Diffusivity.

I. INTRODUCTION

ISOTACHOPHOREIS (ITP) is an electrophoretic separation technique which is based on the difference of migration speed of ionic species under the same electric field. In isotachophoretic separation, the analytes which is to be separated is placed between two electrolytes, namely, the leading electrolyte (LE) and the trailing electrolyte (TE). The LE has the highest mobility and TE is of lowest mobility among the ionic species which are to be separated. When an electric field is applied, the ions of the analytes are arranged in order of their mobilities between the LE and the TE. This consecutive stacking of ions in order of their mobilities is referred as isotachophoresis (ITP). A unique characteristic of ITP is that all species move at the same speed once steady-state has been reached. The cationic or anionic ITP corresponds to stacking of cations or anions, respectively.

In ITP, the electric field adjusts in such a way that each stack of ions with constant electrophoretic mobility migrate at constant speed \( U_{ITP} \) towards the highest mobility zone. The electric field in each stack is constant. This leads to the formation of a plateau shape with sharp interfaces between the adjacent stacks in which step jumps in ion concentration and electric field develop. Kohlrausch [1] proposed a relation based on the conservation of charge with electroneutrality, through which the concentration and electric field in the adjacent zones can be related. The width of the stacked zone and the final concentration of the stacked zone depend on the efficiency of the ITP preconcentration.

ITP is a powerful electrokinetic technique for the concentration, separation, purification and quantification of ionic analytes. In recent years, this technique has been miniaturized and find important applications in the Lab-on-a-Chip technology (Chen et al. [2]). In a recent review article by Gebauer et al. [3] discussions have been made about several potential applications of ITP.

Depending on the amount of the sample present in the system, we can have two modes of ITP namely, peak mode and plateau mode (Garcia-Schwartz et al. [4]). The peak mode ITP arises if the sample zone width is of the order of the interface widths of the adjacent electrolytes, whereas in the plateau mode ITP, the interface widths are negligible compared to the sample zone width. Unlike plateau mode ITP, the sample ionic concentration in a peak mode ITP may vary with the axial position and the sample zone appears a sharp peak between two adjacent electrolytes i.e., LE and TE.

The step changes in electric field and concentration of ions within the interface zones lead to a strong hyperbolic characteristic of the advection-diffusion equations for ion transport. Several authors e.g., Bercovici et al. [5] described the ITP transport as a similar phenomena as shock wave propagation in gas dynamics. In recent years, various high-resolution simulators for one-dimensional computation of ITP have been presented for analyzing electrophoresis separation problems, including SIMUL5, developed by Hruska et al. [6]. Yu et al. [7] applied the space-time Conservation Element and Solution Element (CESE) method to solve 1-D transport equations to accurately resolve the sharp gradients in ITP. In the CESE method, like finite volume method, equations are cast into conservation law form and integrated over a spacetime region. Chou and Yang [8] have provided a detailed discussion on several numerical schemes for simulating ITP and provided the ITP simulation based on flux conservative finite volume scheme in an adaptive grid system. Bercovici et al. (5, 9) developed an efficient numerical solver to resolve the sharp ITP transition zones correctly by using a sixth order compact difference scheme on an adaptive-grid system. Recently, in a review article, Thomann et al. [10] provided a state-of-art on the available computer simulation softwares for ITP separation. However these numerical methods based on 1-D analysis may not be suitable to analyze the peak mode ITP (Khurana and Santiago[11]).

In order to understand the deformation of interfaces in ITP due to an imposed convection, the variables can not be approx-
imated to vary only along the direction of the imposed electric field. A two-dimensional transient behavior of ITP within a channel has been studied numerically by Shim et al. [12]. Their numerical method is based on the first order upwind, hybrid, and power-law finite volume schemes. The effects of cross-sectional change on ITP were studied by Choi et al. [13] through a finite volume method. A finite volume scheme to discretize the spatial derivatives will produce oscillation near the step-jumps in solution. The non-dissipative centered schemes with adaptive grids require a large number of grid points to reduce the spurious oscillation near the step-jump in solutions.

The impact of EOF on isotachophoretic transport of ions was addressed by several authors namely, Saville [14], Schönfeld et al. [15], Bercovici et al. (5, 9), Baier et al. [16], Garcia-Schwarz et al. [4], and the references there-in. The experimental study of Schönfeld et al. [15] shows that sufficiently far away from the ITP transition zones, the velocity of the electrolytes can be considered to be the superposition of EOF velocity with a pressure-driven flow arises due to mismatch of EO velocity of electrolytes. Garcia-Schwarz et al. [4] studied the dispersion of transition zones due to the EOF. The deformation of the transition zones in ITP is due to the convection of electrolytes depends on the the local pressure gradient.

In this paper we have computed the two-dimensional model of ITP within a rectangular channel. The transport of ions is governed by the Nernst-Planck equations. We have considered the effect of wall ζ-potential induced electroosmosis of ions which counterbalance the ITP velocity in anionic ITP. The resolution of the narrow zones involving steep gradients in the electric field and the concentration is a challenge in numerical computation of ITP. The transport of ions are governed by the Nernst-Planck equations coupled with the Navier-Stokes equations for fluid flow and an equation for electric field. The governing equations are discretized through a finite volume method. The advective and electro-migration terms are discretized through an upwind algorithm. Our numerical algorithm can efficiently resolve the sharp ITP interfaces. The present algorithm is tested for accuracy by comparing it with the steady-state analytical solution for ideal ITP transport. We have measured the dispersion through the second-order moment analysis of the ionic species. The area averaged ionic distribution of our computed solution is found to agree well with the Taylor-Aris dispersion model for lower values of the convection speed.

II. MATHEMATICAL MODEL

We assume the electrolytes to consists of monovalent trailing electrolyte (TE) of anionic concentration $C_{-}^{+}$, monovalent leading electrolyte (TE) of anionic concentration $C_{-}^{-}$, the anionic concentration of sample species is $C_{s}$ and a common cation concentration of $C_{o}$. The migration of charged species in an electrolyte under an external electric field is governed by diffusion and electromigration. We consider x-axis along the channel and y-axis perpendicular to it. The mass conservation of the ionic species leads to the following Nernst-Planck equation.

$$\frac{\partial C_i}{\partial t} + \nabla.N_i = 0$$  \hspace{1cm} (1)

where $i = +, s$ or $-$. Here subscript + refer the TE anions, - for the LE anions and $s$ for the sample anions. The concentration of common ion $C_{0}$ is obtained through electro-neutrality assumption i.e., $C_{0} = \sum C_i$. The molar flux of $i^{th}$ species is

$$\vec{N}_i = -D_i \nabla C_i + C_i (\vec{q} + z_i \mu_i \vec{E})$$  \hspace{1cm} (2)

where valance $z_i = -1$ for anions and $z_0 = +1$ for common cation. The mobility and diffusivity are related via Nernst-Planck equations coupled with the Navier-Stokes equations for fluid flow and an equation for electric field. The electric field will vary. At steady state in ideal ITP ( without any convection), all the species will migrate at the same ITP velocity $U_{ITP}$. Due to the distinct electrophoretic mobility of each ionic species, the electric field strength of each zone will be different. The electric field in each zone is adjusted so that the zones migrate at a constant speed, $U_{ITP}$. If $E_i$ ($i = +, s$ or $-)$ are the strengths of electric field in each separated zone occupied by only one species, then using the relation $U_{ITP} = \mu_i E_i$ we get

$$E_i = E_0 \frac{1/\mu_i}{\sum (l_i/|\mu_i|)}$$  \hspace{1cm} (5)

where the summation is taken over all the species and $l_i$ is the portion of the length $L$ which is filled by $i^{th}$ species. We can also express $E_{-}$ and $E_{+}$ in terms of the applied current density $j_0$ as follows

$$j_0 = F(\mu_{-} + \mu_0)C_{s}^{-}E_{-} = F(\mu_{+} + \mu_0)C_{s}^{+}E_{+}$$

$$= F(\mu_{+} + \mu_0)C_{s}^{+}E_{+}$$  \hspace{1cm} (6)

From the fact that at steady state all species moves at a constant speed $U_{ITP} = \mu_i E_i$, the above relation leads to the relationships for the bulk concentration of TE, LE and all the sample species as

$$\frac{C_{s}^{-}}{C_{s}^{+}} = \frac{\mu_{+} + \mu_0}{\mu_{-} + \mu_0} \frac{\mu_{-}}{\mu_{+}}$$

$$\frac{C_{s}^{-}}{C_{s}^{+}} = \frac{\mu_{+} + \mu_0}{\mu_{-} + \mu_0} \frac{\mu_{-}}{\mu_{+}}$$  \hspace{1cm} (7)
where suffix \( \infty \) stands for the bulk value of the concentrations.

We consider the height \( H \) of the channel as the length scale and \( U_{ITP} \) as the scale for velocity. The concentration of ionic species are scaled by the bulk concentration of LE i.e., \( C_{i}^{p} \), potential by \( \phi_i = RT/F \) and time is scaled by \( \tau = H/U_{ITP} \). The Nernst-Planck equations in nondimensionalized form can be written as

\[
\frac{\partial c_i}{\partial t} + (\mathbf{u} \cdot \nabla) c_i = -z_i D_{i} \frac{1}{P_e} \nabla \cdot (c_i \nabla \phi) = \frac{D_{i}}{P_e} \nabla^2 c_i \quad (8)
\]

where \( D_i \)’s are the diffusivities of the respective ions and Pecllet number \( P_e = U_{ITP} H / D_i \).

The charge conservation equation in nondimensional form is as follows

\[
\nabla \cdot \left[ \left( c_i + D_{+} + D_{-} - D_{0} \right) \nabla \phi \right] = - \left( \frac{z_i D_{+}}{D_{0} + D_{0}} \right) \nabla \phi \quad (9)
\]

\[
\nabla^2 \left[ c_i + \frac{z_i D_{+}}{z_i D_{+} + z_i D_{-}} \nabla \phi \right] = \frac{z_i D_{+}}{z_i D_{+} + z_i D_{-}} \nabla \phi \quad (9)
\]

where \( z_i \) is the charge of the ionic species, \( D_{0} \) is the diffusion coefficient of the solvent, \( D_{+} \) and \( D_{-} \) are the diffusion coefficients of positive and negative ions, respectively, and \( \nabla \) is the gradient operator.

The impact of electroosmosis of electrolytes on ITP transport is significant when the electrophoretic mobility of each zone is different. The bulk concentration of LE is considered to be \( C_{\infty} \) so that the Debye layer thickness \( (O \sim 10 \mu m) \) becomes much lower than the height of the channel considered here \( (H \geq 25 \mu m) \). Thus, the slip velocity condition can be assumed on the channel wall. We denote the electrolyte slip velocity along the wall for each of three zones as \( u_{i}^{EOF} \) (i.e., + and 0) respectively. The slip velocity \( u_{i}^{EOF} \) is determined by the Helmholtz-Smoluchowski’s equation

\[
u_{i}^{EOF} = \frac{\zeta_{i} E_{i}}{|\eta|} \quad (15)
\]

where \( \zeta_{i} \) is the zeta potential and \( \mu_{i}^{EOF} \) is the electrophoretic mobility. The difference in EOF velocity of the electrolytes induces a locally uniform, but not globally, axial pressure gradient. Sufficiently far away from the transition zones, the velocity of the ionic species is considered to be the superposition of EOF velocity and Poiseuille flow due to a constant pressure gradient [15] as

\[
u_{i}(y) = u_{i}^{EOF} + 6u_{p,u} \frac{y(1-y)}{H^2} \quad (11)
\]

where \( u_{p,u} \) is the average flow due to a constant pressure gradient on the \( \eta \)th zone. If the net pressure drop across the length \( L \) is zero, then \( \sum_{\eta} u_{p,u} = 0 \) along with the conservation of mass leads to

\[
u_{i}(y) = u_{i}^{EOF} + 6\nu_{p,E} \frac{y(1-y)}{H^2} \quad (12)
\]

The average electroosmotic speed \( \bar{u} \) is assumed to counterbalance the ITP velocity. Thus,

\[
u_{p,E} = \sum_{\eta} u_{i}^{EOF} = U_{ITP} \quad (13)
\]

The slip velocity along the wall is

\[
u_{i}^{EOF}(x; y = 0, H) = \mu_{i}^{EOF}(x; y = 0, H) \quad (14)
\]

where \( \mu_{i}^{EOF}(x; y = 0, H) \) are the wall mobility and axial electric field on the wall at different axial position \( x \). The approximate wall mobility is given by [16]

\[
u_{i}^{EOF}(x; y = 0, H) = \mu_{i}^{EOF}(x; y = 0, H) \quad (15)
\]

where \( C_{i}(x; y = 0, H) \) and \( \mu_{i}^{EOF} \) are the concentration values on the wall and electroosmotic mobilities of the \( i \)th ionic species respectively.

The velocity field \( \mathbf{q} \) due to the mismatch of EOF is governed by the nondimensional Navier-Stokes equations as

\[
u \frac{\partial \mathbf{q}}{\partial t} + (\mathbf{q} \cdot \nabla) \mathbf{q} = -\frac{1}{Re} \nabla p + \frac{1}{Re} \nabla^2 \mathbf{q} + B \nabla \phi \nabla^2 \phi \quad (16)
\]

and

\[
\nabla \cdot \mathbf{q} = 0 \quad (17)
\]

where \( \mu, \eta \) and \( \rho \) are the fluid pressure, viscosity and density, respectively. This electrical stress arises due to the spatial variation of \( \phi \) across the channel. The nondimensional quantity \( B = (\epsilon_{r} \phi_{0}^{2} / |\eta| D X) / Re U_{ITP} \) with \( Re = \rho U_{ITP} H / \mu \) and \( \mu U_{ITP} / H \) is the pressure scale.

We solve the Navier-Stokes equations, which are coupled with the ion concentration and electric field equations, subjected to those prescribed boundary conditions to determine the convective velocity of ions in the transition zone.

Here we have considered a 400 \( \mu m \) long channel containing 40 \( \mu m C_{\infty} \) amount of sample sandwiched between LE and TE. The TE and LE are taken to be symmetrically placed. To make the quantitative measurement using this model, the electrophoretic mobilities of all species, concentration of the leading electrolyte, voltage drop across the channel and height of the channel must be specified. We have taken \( \phi_{0} = 0.32586V \), \( \epsilon_{r} = 6.0939 \times 10^{-12} C/V m \), \( K_B = 1.831 \times 10^{-28} J / K \), \( e = 1.602 \times 10^{-19} C \), \( T = 300 K \), \( \mu = 10^{-3} Pa S \) and \( \rho = 10^3 kg/m^3 \).

III. NUMERICAL METHODS

We have computed the equations for ion transport and electric field in a coupled manner through the finite volume method. The computational domain is subdivided into a number of control volumes. In this method, the equations cast into conservative form, are integrated over each control volumes. The variables, such as electric potential and ionic concentrations are stored at the cell centers. This approach enables to
compute the jump discontinuity as part of the solution. Due to the hyperbolic nature of ion transport equations, discretization of the convective flux and electromigration terms at the cell interfaces through a linear interpolation of variable values between two neighbors on the either side of the control volume interfaces, may lead to a numerical instability. In order to resolve the sharpness of the variables, which occurs in ITP interface, we adopt the upwind scheme QUICK (Quadratic Upwind Interpolation Convection Kinematics) to discretize the electromigration and convection terms in the ion transport equations. The QUICK scheme uses a quadratic interpolation/extrapolation between three nodal values to estimate the variables at the interfaces of each cell. The diffusion fluxes at the control volume interfaces are estimated by linear interpolation between two neighbors to the either side of the control volume interfaces.

We use an implicit scheme to discretize the time derivatives. At time level, we use an iterative procedure for the computation of ion transport equations as these equations are coupled with the charge conservation equation. The iteration procedure starts with an assumption for potential at each cell. At every iteration, the electric field is determined by solving the reduced elliptic equation for charge conservation equation, i.e., equation (9). The elliptic equation (9) is solved by a line-by-line iterative method along with the successive-over-relaxation (SOR) technique. The iterations are continued until the absolute difference between two successive iterations become smaller than the tolerance limit $10^{-6}$ for concentration as well as potential distribution across the channel.

For the case of EOF impact on ITP, the fluid flow equations which are coupled with the mass transfer equation and the equation for electric field, are computed by using a control volume approach [17] over a staggered grid system. In the staggered grid system the velocity components are stored at the cell interface to which it is normal. Here we also used the QUICK scheme to discretize the convective terms. The governing discretized equations are solved through a pressure correction algorithm, SIMPLE [17]. The pressure link between two neighbors to the either side of the control volume interfaces through a linear interpolation of variable values at the cell interface to which it is normal. Here we also used the QUICK scheme to discretize the convective terms. The governing discretized equations are solved through a pressure correction algorithm, SIMPLE [17]. The pressure link between two neighbors to the either side of the control volume interfaces is accomplished by transforming the discretized continuity equation into a Poisson equation for pressure correction.

At the end of every iteration, the velocity on the channel wall is obtained by (14) using the updated values for concentration distribution and electric field. The iteration at each time step is continued until the divergence-free velocity field is obtained. However for this purpose, the divergence in each cell is towed below a pre-assigned small quantity.

A steady state solution is achieved by taking sufficient time steps until the concentrations and velocity field remains unchanged with time. The initial condition for dispersed ITP is governed by the solution of the corresponding ideal ITP case. In order to test the accuracy of our algorithm, we have compared the computed ideal ITP results with the analytical solutions and found them in good agreement (Fig. 1a, b).

### IV. RESULTS AND DISCUSSIONS

In order to check the time dependency of concentration profile for ideal ITP, computed result for the logarithmic ratio of the concentrations of LE and TE is compared with the analytical solution given by Goet et al.[18]. The results show (Fig. 1a) that the concentration distribution becomes steady after a short transition with respect to a coordinate comoving with the ITP interface. Here the solid line represent the analytical solution and the dotted lines are the computed solutions for different non-dimensional time.

We investigated the dependence of LE-TE transition zone width on mobility ratio ($D_{+}/D_{-}$) is presented in Fig. 1b. The transition zone is the over-lapped region in which the concentration field of dissolved ions changes from their zone characteristic value to zero. The overlapping can be minimized by increasing the electric field ($E_{0}$) and/or decreasing the mobility ratio ($D_{+}/D_{-}$). Our computed values for transition zone length are compared with the expression provided by MacInnes and Longsworth [19], and found them to be in good agreement. It may be noted that at high mobility ratio at a fixed $D_{+}$, the diffusion effect becomes stronger. In ITP, electromigration leads to sample stacking and diffusion works against it. The narrow width of the transition zone during separation has a significant meaning in ITP separation.

The profile for ionic species concentration in steady-state ITP in absence of an imposed convection (ideal ITP) with respect to a reference frame moving with the ITP velocity is presented in Fig. 2a-c for different values of the electrophoretic mobility ratio of the sample ion. The penetration of sample electrolyte into LE or TE zone strongly depends on its mobility. Figs. 2 shows that as the mobility ratio between the sample and LE increases and consequently, the mobility ratio between TE and sample decreases, the sample penetrates more into the LE zone and vice versa. The interface region between the LE-sample (or sample-TE) becomes sharp compared to the TE-sample interface as the sample mobility becomes close to the LE (or TE). Consequently, the TE-sample (sample-LE) interface becomes smaller compared to the width of the LE-sample (TE-sample) interface zone.

We now present results for steady-state isochrophoresis of analytes which is interacted with EOF. The average EOF of analytes is assumed to be equal and opposite to the ITP velocity. In this situation, a steady state is achieved in a stationary frame of reference after a short transient stage. The sample distribution in steady state is shown in Fig. 3a,b for different values of the electroosmotic mobility of LE and TE. The initial amount of sample and its electrokinetic properties is considered to be same in all the cases. We have varied the EO mobilities of LE and TE keeping the electrophoretic mobility ratio of LE-to-TE i.e., $k_1 = \mu_-/\mu_+ = 3$. It is evident that the sample zone is dispersed due to the EO convection. The sharpness in the ITP transition zones is smeared out due to the imposed convection. The form of the transition zone depends on the local axial pressure gradient. Depending on the EO mobility of LE and TE, the pressure gradient in the transition zones may become adverse or favorable. We have measured the dispersion of the transition zone for wide range of LE-to-TE electrophoretic mobility ratio. We find that the dispersion in transition zone is highest for the cases in which the electrophoretic mobility of the sample is either close to LE or TE for a given value of EO mobility of electrolytes. It...
may be noted that the EO mobility of electrolytes satisfy the relation (13). The dispersion is measured through the second-order moment analysis. For the sake of brevity we have not presented the results for dispersion.

We have compared the area-averaged computed solution of the analyte concentration with the 1-D model based on the Taylor-Aris effective diffusion coefficient. The effective diffusivity of each ionic species is obtained by

$$D_{\text{eff},i} = D_i \left[ 1 + \beta \left( \frac{H u_p}{D_i} \right)^2 \right]$$

(18)

where i= +, s, or - and $u_p = \text{Max} \ u_{p,i}$. For a parallel plates channel the value of the constant $\beta$ is 1/210. The area averaged concentration distribution of ions ($\overline{C}_i$) in the 1-D Taylor-Aris dispersion model is governed by

$$\frac{\partial \overline{C}_i}{\partial t} + \frac{\partial}{\partial x} \left[ \left( z_i \mu_i E_x \overline{C}_i - D_{\text{eff},i} \frac{\partial \overline{C}_i}{\partial x} \right) - U_{\text{ITP}} \overline{C}_i \right] = 0$$

(19)

Our computed solutions for the 2-D dispersed ITP are found to be in good agreement with this 1-D model (Fig.4a,b). The width of the sample zone is perfectly captured by the 1-D model based on the Taylor-Aris effective diffusivity.
Fig. 3. Concentration distribution of sample species for fixed $k_1(\mu_+/\mu_+ = D_+/D_+) = 3$ and $k_2(\mu_-/\mu_+ = D_-/D_+) = 2$. The results are for channel height $H = 25\mu m$. The electrophoretic diffusivity of LE is taken as $D_+ = 7.0 \times 10^{-10}m^2/Vs$ with $C^\infty = 0.01M$ and $E_0 = 10^8V/m$. The electroosmotic mobility of the ionic species are considered as (a) $\mu_{EOF} = 2.54 \times 10^{-8}m/Vs$, $\mu_{EOF} = 2.54 \times 10^{-8}m/Vs$, $\mu_{EOF} = 8.54 \times 10^{-8}m/Vs$, $\mu_{EOF} = 2.94 \times 10^{-9}m/Vs$, $\mu_{EOF} = 7.36 \times 10^{-5}m/Vs$, $\mu_{EOF} = 9.82 \times 10^{-9}m/Vs$.

Fig. 4. Area averaged concentration distribution of sample species for fixed $k_1(\mu_+/\mu_+ = D_+/D_+) = 3$ and $k_2(\mu_-/\mu_+ = D_-/D_+) = 2.0$ along the axis of the channels. The results are for channel height $H = 25\mu m$. The results are for channel height $H = 25\mu m$. The electroosmophic diffusivity of LE is taken as $D_+ = 7.0 \times 10^{-10}m^2/Vs$ with $C^\infty = 0.01M$ and $E_0 = 10^8V/m$. The electroosmotic mobility of the ionic species are considered as (a) $\mu_{EOF} = 2.54 \times 10^{-8}m/Vs$, $\mu_{EOF} = 2.54 \times 10^{-8}m/Vs$, $\mu_{EOF} = 8.54 \times 10^{-8}m/Vs$, $\mu_{EOF} = 2.94 \times 10^{-9}m/Vs$, $\mu_{EOF} = 7.36 \times 10^{-5}m/Vs$, $\mu_{EOF} = 9.82 \times 10^{-9}m/Vs$.

V. CONCLUSIONS

We have investigated the situations in which electromigration in isotachophoresis is balanced by the average electroosmotic velocity of electrolytes. Our results show that a stationary zone of ITP stack results. However, the EOF reduces the resolution of ITP transition zones and produces strong dispersion on the sample stack. The numerical algorithm presented here can resolve accurately the transition zones in peak mode as well as plateau mode for ideal ITP. The deformation of the sample zone when ITP is interacted with EOF depends on the local pressure gradient. The induced pressure gradient develops due to mismatch of EO velocity of electrolytes. Another key result of this study is that a 1-D area-averaged model for the sample distribution based on Taylor-Aris dispersion agrees well with the more detailed 2-D model.

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