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Review

# Capillary electrochromatography: theories on electroosmotic flow in porous media

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**Abstract**

In view of the present interest in capillary electrochromatography (CEC), theories dealing with electroosmotic flow (EOF) in porous media are reviewed with particular regard to the use of packed capillaries in CEC. Two of the models found in the pertinent literature are applicable to CEC and give simple analytical solutions. The first of the two models is based on von Smoluchowski's work as adapted and extended by Overbeek. It deals with EOF through packed capillaries under conditions of low electric field strength where the EOF varies linearly with the field strength because there is no polarization of the double layer. Overbeek's model originally developed for porous media of infinite dimensions was modified in an attempt to account for the wall effect that assumes importance in the packed capillary columns used in CEC. The second model proposed by Dukhin and his coworkers predicts EOF of at least an order of magnitude higher than that expected by classical theories. This "electroosmosis of the second kind" is believed to occur in columns packed with conductive particles like ion exchangers at high electric field strengths when the double layer is polarized and the EOF becomes a non-linear function of the applied voltage. Conditions necessary for electroosmosis of the second kind are likely to arise upon the further development of CEC when further enhancement of the speed of analysis is brought about at electric field strength higher than that employed at present. © 1997 Elsevier Science B.V.

*Keywords:* Electrochromatography; Reviews; Electroosmotic flow

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## 1. Introduction

Capillary electrochromatography (CEC) has the potential to become another high-performance liquid chromatographic technique that employs packed capillary columns and high electric field so that the mobile phase is driven by electrosmotic flow[1] (EOF) and is carried out in apparatus similar to that used in CZE. The mixed separation mechanism of CEC is borrowed from both HPLC and CZE [1]. The history of CEC could be traced to almost 60 years back when Strain [2,3] applied electric field across an adsorption column to demonstrate higher selectivity due to combination of electrophoretic and chromatographic separation forces. Almost thirty years later in 1974, Pretorius et al. suggested the use of EOF as "pumping mechanism" alternative to pressure driven flow in order to expand the scope of the then newfangled technique of HPLC [4]. The viability of CEC in packed capillary columns was demonstrated by Jorgenson and Lukacs in 1981 [5] and examined in some detail by Knox and Grant in 1987 [6]. Recently several research groups have made contributions to the further development of this separation technique [7–21].

One of the characteristic features of CEC is the usage of high electric field across the column in lieu of the high column inlet pressure utilized traditionally in HPLC. This offers a simple means to attain in capillary columns packed with very small particles, flow rates so high that they would require a prohibitively high pressure drop in HPLC. In order to exploit the potential of CEC, control and optimization of electrochromatographic conditions to generate high EOF velocities are of the utmost importance. Theoretical understanding of the EOF and the associated transport phenomena in porous media such as packed columns in CEC would require an exact solution of the flow field in porous media under conditions prevalent in CEC by simultaneously solving the Poisson–Boltzmann and Navier–Stokes equations, a daunting task despite recent expeditious advancements in computing power.

The literature on electrokinetic phenomena is very large and mainly addresses theoretical problems. Yet, only a scant number of papers dealing with EOF in porous media has been found. The goal of the present work is to review two of the models found on this topic that yield simple but relevant analytical solutions. They deal with the hydrodynamics and the enhancement of EOF and are presented in a form adapted to the CEC environment. The first model is based on prior work of Overbeek and Wijga [22–24] which is rooted in the flat plate model by von Smoluchowski, and deals with the hydrodynamics of EOF through beds packed with non-conducting particles at electric fields low enough so that there is no polarization of the double layer. Since in the works of Pretorius et al. [4], Jorgenson and Lukacs [5] as well as by Knox and Grant [6,8] this model has been applied to CEC, present thinking on the generation and the magnitude of EOF in CEC is largely determined by this model. The second and more recent model which departs from the classical Smoluchowskian view, originates from Dukhin's group [25–29]. It deals with "electrosmosis of the second kind" that occurs when the particles are conducting and the electric field is high enough to cause polarization of the double layer.

In view of the great present interest in CEC, we hope that this review reveals the complexity of the electrokinetic phenomena underlying EOF in porous media and will stimulate the experimental and theoretical work necessary for an understanding of the physicochemical basis of CEC and to develop this technique into a powerful analytical tool.

## 2. The von Smoluchowski equation

In his treatment of liquid movement adjacent to a flat, uniformly charged surface under the influence of electric field acting parallel to the interface, von Smoluchowski [30] examined the balance between viscous and electrical forces and arrived at the following expression for $u_w$, the EOF velocity along the surface,

$$u_w = -\frac{\varepsilon\varepsilon_o\zeta_w E}{\eta} \quad (1)$$

where, $\varepsilon$ is the dielectric constant of the medium, $\varepsilon_o$ is the permittivity of the vacuum, $E$ is the applied

[1] For the sake of brevity the words "electrosmosis" and "electrosmotic" suggested by von Smoluchowski [30] are used here.

electric field and $\eta$ is the viscosity of the bulk solution. $\zeta_w$ is the zeta potential, defined as the potential at a hypothetical 'plane of shear' [23].

Von Smoluchowski also suggested that an equation similar to Eq. (1) may hold true for the case of a porous plug or membrane, regarding them as a collection of Poiseuille tubes [31]. Several treatments for EOF in capillaries are based on similar assumptions as that by von Smolukhowski.

## 3. Overbeek's model for EOF in porous media

The following analysis is based on Overbeek and Wijga's work [22–24] and is valid for porous/non-porous packing particles of any arbitrary shape. The assumptions are that the particles be non-conducting, have uniform zeta potential and a double layer thin compared to the radius of the pores in the plug. Overbeek upon integration over the whole interstitial volume of the bed obtained the following expression for the average velocity

$$< u_p > = \frac{1}{V_c} \int_{V_{cf}} u_p \, dV_c = - \frac{\varepsilon \varepsilon_o \zeta_p}{\eta V_c} \int_{V_{cf}} E dV_c \qquad (2)$$

where, $\zeta_p$ is the zeta potential at the surface, $V_c$ and $V_{cf}$ are the total column volume and the volume of the interstitial space, respectively. The integration is performed over $V_{cf}$ only since flow is only in the interstices. $u_p$ is electrosmotic velocity that is generated locally at the packing surface and is given by an expression similar to Eq. (1), which describes Smoluchowski's equation for EOF generated at the wall, as follows

$$u_p = - \frac{\varepsilon \varepsilon_o \zeta_p E}{\eta}. \qquad (3)$$

For the current, $j$, the following relationship holds

$$j = \sigma^* E = \frac{\sigma_b}{V_c} \int_{V_{cf}} E dV_c \qquad (4)$$

where, $\sigma^*$ and $\sigma_b$ are the conductivities of the packed column and the open tube, both filled with the electrolyte solution, respectively. Combination of Eq. (2) and Eq. (4) yields the average velocity as

$$< u_p > = - \frac{\varepsilon \varepsilon_o \zeta_p E}{\eta} \left( \frac{\sigma^*}{\sigma_b} \right) \qquad (5)$$

with the conductivity ratio, $\sigma^*/\sigma_b$, that is readily determinable experimentally.

Eq. (5) was derived by Overbeek [23] to describe EOF in a porous medium without boundaries. According to experimental findings [32], in CEC with packed capillaries the contribution of the capillary inner wall, which may be neutral or charged, to the EOF cannot be ignored. In order to account for the "wall effect" the Overbeek model will be extended to evaluate the contributions of the wall and the packing to EOF under conditions employed in CEC.

### 3.1. Charged capillary wall and neutral packing

It is assumed that the EOF is generated only at the charged wall and the packing particles are uncharged. The flow can then be visualized in the form of very thin annuli of liquid in the packed column. Each annulus faces a force in the forward direction (the direction of EOF) from the annulus enveloping it and a force in the backward direction from the annulus inside it. The inertia terms and the compressibility of the fluid are assumed to be negligibly small. The net viscous force, $F_v$, on such an annulus of unit volume in the absence of any particles is given by

$$F_v = \frac{\eta}{r} \frac{d}{dr} \left( r \frac{du_{rw}}{dr} \right) \qquad (6)$$

where, $r$ is the radial coordinate and $u_{rw}$ is the local velocity in the axial direction.

In such a column with charged tube wall and uncharged packing, the flow velocity would be a rapidly fluctuating function of radial position with zero value at the surface of the uncharged particle and maximum in the intraparticular space. Hence, the velocity under consideration, $u_{rw}$, is more like a volume average velocity. Besides the viscous forces, the fluid in the shell also experiences a drag force from the packing particles in the shell. The total drag force, $F_d$, offered by spherical packing particles of diameter $d_p$ that are located far enough from each other to act like isolated spheres, is given by the product of the drag force by an isolated sphere and

the number of spherical particles in a shell of unit volume as follows

$$F_d = (6\pi\eta d_p u_{rw})\left(\frac{1-\varepsilon_c}{4\pi d_p^3/3}\right) \quad (7)$$

where $\varepsilon_c$ is the total porosity of the column. Since in packed columns the particles are in close contact with each other, the actual drag force is different than that given by Eq. (7). This is corrected for by introducing the dimensionless packing parameter, $\alpha$, which depends on the structure of packing and shape of the particles and should be easily determinable from experimental data. Performing the balance between the viscous and the drag forces and simplifying the equations we have that

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{du_{rw}}{dr}\right) = \frac{9}{2}\frac{\alpha(1-\varepsilon_c)u_{rw}}{d_p^2} = \frac{\beta^2}{d_p^2}u_{rw} \quad (8)$$

where $\beta$ is another dimensionless constant that is readily evaluated if $\alpha$ and $\varepsilon_c$ are known from the following relationship

$$\beta = 3\sqrt{\frac{\alpha(1-\varepsilon_c)}{2}}. \quad (9)$$

The boundary conditions for solving the differential equation as given in Eq. (8) are

$$\frac{du_{rw}}{dr} = 0 \quad \text{at } r = 0 \quad (10)$$

and

$$u_{rw} = u_w \quad \text{at } r = R \quad (11)$$

where, $u_w$ is the EOF velocity at the wall as given by Eq. (1). Eq. (11) simply reflects no slip condition at the plane of shear that is very close to the tube wall for thin double layers.

Solution of the system of Eqs. (8)–(11) for the potential distribution can be found in the literature [33,34] and written for the local velocity as

$$u_{rw} = u_w\left[\frac{I_o(\beta r/d_p)}{I_o(\beta R/d_p)}\right] \quad (12)$$

where, $I_o$ is the Bessel's function of the zeroth order.

For $\beta r/d_p$ greater than 3.5, which is generally the case, the zeroth order Bessel's function can be approximated by

$$I_o(\beta r/d_p) = \frac{e^{\beta r/d_p}}{\sqrt{2\pi\beta r/d_p}} \quad (13)$$

which in turn can be substituted back into Eq. (12) to give the simplified solution as

$$u_{rw} = u_w\left[\frac{e^{\beta r/d_p}}{\sqrt{2\pi\beta r/d_p}}\frac{\sqrt{2\pi\beta R/d_p}}{e^{\beta R/d_p}}\right] = u_w\left(\sqrt{\frac{R}{r}}\right)e^{\beta(r-R)/d_p}. \quad (14)$$

Eq. (14) for the region close to the wall is illustrated in Fig. 1. The flow velocity is maximum at the plane of shear and then decays quickly as we move away from the wall. This should not be surprising as in a column packed with uncharged particles, EOF is generated at the tube wall and the interior of the tube contributes only the drag resistance. It should be noted that the flow velocity falls to 70% of its maximum value as soon as we move a distance of one particle diameter away from the column wall.

The average velocity in the column for the above case can be easily determined using the velocity profile given in Eq. (17) and accounting for the tortuosity in the bed as follows

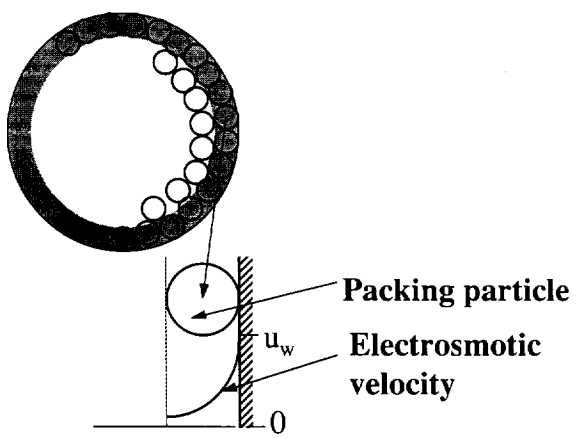


Fig. 1. Schematic illustration of loci of the wall effect where EOF decays in the case of charged tube wall and uncharged packing particles.

$$< u_{rw} > = \frac{\int_0^R 2\pi r u_{rw}\, dr}{\pi r^2}\left(\frac{\sigma^*}{\sigma_b}\right)$$

$$= u_w\left(\frac{\sigma^*}{\sigma_b}\right)\left(\frac{2}{R^2 I_o(\beta R/d_p)}\right)\int_0^R r I_o(\beta r/d_p)\, dr \quad (15)$$

In order to simplify Eq. (15) we need to use the property that the zeroth and first order Bessel's functions are related by

$$\int_0^{\beta R/d_p} r I_o(r)\, dr = \frac{\beta R}{d_p} I_1(r) \quad (16)$$

and for $\beta r/d_p$ greater than 3.5 by

$$I_o(\beta r/d_p) = I_1(\beta r/d_p) \quad (17)$$

Using Eqs. (15)–(17) and performing some algebraic simplifications we get the expression for the average velocity as

$$< u_{zw} > = u_w\left(\frac{\sigma^*}{\sigma_b}\right)\left(\frac{2}{\beta R/d_p}\right). \quad (18)$$

Eq. (18) suggests that the average velocity in the packed column varies linearly with the dimensionless particle diameter, $d_p/R$.

### 3.2. Extended Overbeek's model to CEC

Under conditions employed in CEC, the EOF is generated not only at the capillary wall but also at the surface of the packing. According to Overbeek [22–24], the flow through a column packed with charged particles is visualized as flow through several parallel tubes with the zeta potential of the wall being equal to that of the particles. The velocity in each of such tubes is given by the von Smoluchowski's equation which was adapted by Overbeek to arrive at Eq. (5) and thus account for the tortuosity and other characteristics of the porous medium by the conductivity ratio.

When the zeta potential of the wall is the same as the packing ($\zeta_w = \zeta_p$), the velocity profile should be flat according to Overbeek's expression in Eq. (5). For the case when the zeta potentials at the tube wall and the particle surface are not equal, the total velocity could be evaluated by adding a term to Overbeek's velocity expression to account for the wall effect. This term would be given for the local and average velocities by Eq. (14) and Eq. (18) with the zeta potential of the wall being replaced by the "excess zeta potential" on the wall ($\zeta_w - \zeta_p$) that is responsible for the wall effect, i.e.

$$u_r = u_{rw}\left(1 - \frac{\zeta_p}{\zeta_w}\right) + u_p$$

$$= u_p\left[1 + \left(\sqrt{\frac{R}{r}}\right)e^{\beta(r-R)/d_p}\left(\frac{\zeta_w}{\zeta_p} - 1\right)\right] \quad (19)$$

where, $u_r$ is the net local velocity from both contributions. Fig. 2 illustrates the effect of the magnitude of the excess zeta potential on the radial profile of the EOF velocity. The plots show that the wall effect is limited to a narrow annulus at the wall that increases in width with the magnitude of the excess zeta potential.

The effect of particle diameter on the radial flow

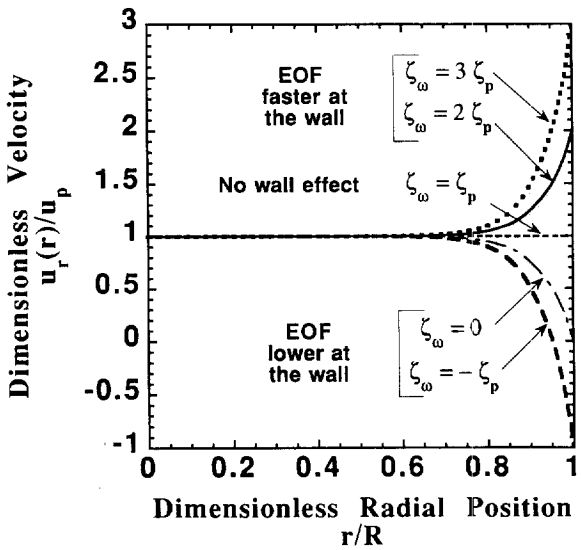


Fig. 2. Graphs illustrating the hypothetical radial flow distribution according to Eq. (19) when both the tube wall and the packing are charged. The ratio of zeta potentials of the wall and the particles in the packing ($\zeta_w/\zeta_p$) is the parameter. The velocity is made dimensionless by using the local electrosmotic velocity at the particle surface as the reference. Conditions; $R = 50$ μm; $\varepsilon = 0.4$ and $d_p = 5$ μm.

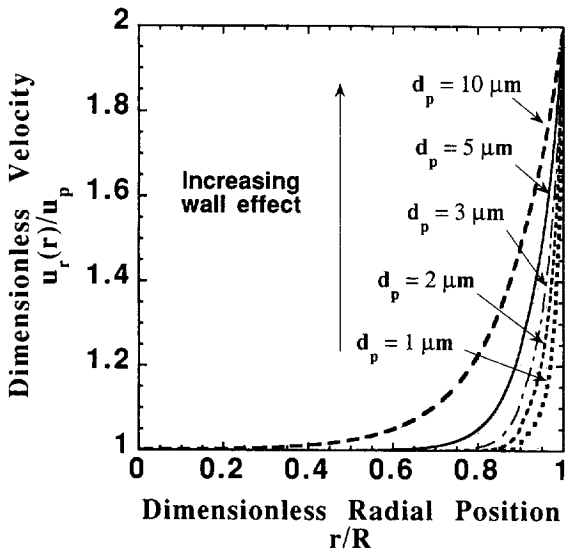


Fig. 3. Graphs illustrating the hypothetical radial flow distribution according to Eq. (19) when both the tube wall and the packing are charged with the particle diameter as the parameter. The velocity is dimensionless by using the local electrosmotic velocity at the particle surface as the reference. Conditions; $R = 50$ μm; $\varepsilon = 0.4$ and $\zeta_w = 2\zeta_p$.

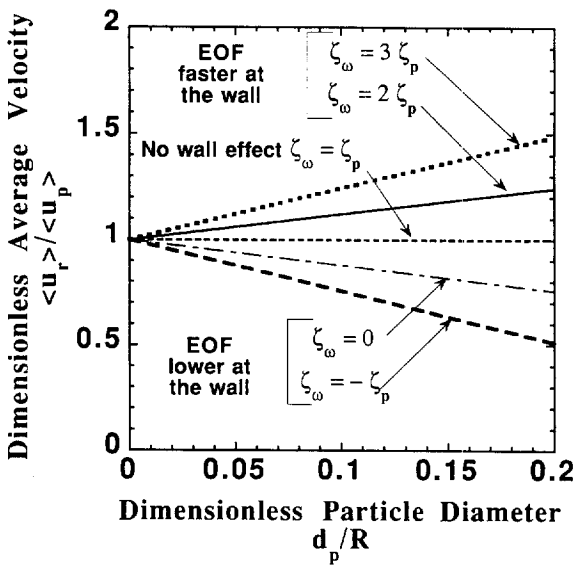


Fig. 4. Illustration of the effect of the packing particle diameter on the average flow velocity for the case of charged tube and packing. For making the velocity dimensionless the average electrosmotic velocity defined by Overbeek, cf. Eq. (5), was used as the reference. Conditions; $R = 50$ μm and $\varepsilon = 0.4$.

profile is illustrated in Fig. 3 for certain typical cases. It is seen that the wall effect increases with the particle diameter of the packing for fixed tube diameter. This is because with increasing particle diameter, the area of the one particle diameter thick annulus relative to the total cross-sectional area increases and so the effect becomes more evident.

By integrating Eq. (19) over the bed volume we obtain the expression for the average velocity in the column as

$$<u_r> = <u_{rw}>\left(1 - \frac{\zeta_p}{\zeta_w}\right) + <u_p>$$

$$= <u_p>\left[1 + \left(\frac{d_p}{R}\right)\left(\frac{2}{\beta}\right)\left(\frac{\zeta_w}{\zeta_p} - 1\right)\right]. \qquad (20)$$

The variation of the average velocity as a function of the particle diameter is illustrated in a dimensionless graph with the excess zeta potential as the parameter in Fig. 4. As mentioned above, the wall effect would be palpable only in the case when the two zeta potentials are unequal and then increase with the magnitude of the difference. As the particle diameter increases, the wall effect increases too.

## 4. Dukhin's model of electrosmosis of the second kind

Dukhin's group [25–29] proposed a model for "electrosmosis of the second kind", that is characterized by an unexpectedly high EOF velocity when the particles have higher conductivity than the electrophoretic medium. Dukhin's experiments with ion exchanger particles under sufficiently high electric field strengths demonstrated the generation of high EOF that was explained by the induction of bulk charge in the surrounding electrolyte solution.

This explanation is based on the assumption that the tangential and the normal component of the electric field at the surface of a curved ion exchanger as shown in Fig. 5, induces bulk charges through different mechanisms as described in the following two sections.

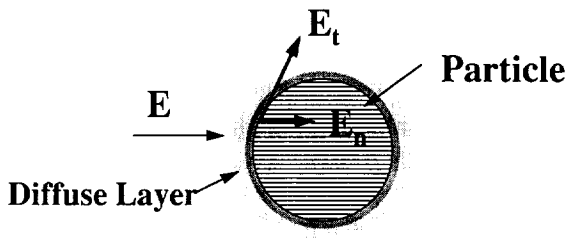


Fig. 5. Schematic illustration showing the normal and tangential components of the electric field acting on the diffuse layer at a charged curved surface.

### 4.1. Differential permeation of the particle by the counterions

Fig. 6 shows the effect of the normal component of the electric field, $E_n$, across a negatively charged ion-exchanger, the surface of which is permeable to the counterions, immersed in an electrolyte solution. The negative ions are repelled by the negatively charged surface and therefore their diffusive flux from the bulk solution toward the surface is counterbalanced by their electromigration in the opposite direction [25] so that

$$-D^- \frac{dc^-(x)}{dx} - D^- c^-(x) \frac{e}{kT} \frac{d\psi(x)}{dx} = 0 \qquad (21)$$

where, $e$ is the elementary charge, $k$ is the Boltzmann constant, $T$ is the absolute temperature of the electrolyte, $\psi$ is the electrical potential, $D^-$ is the diffusivity of the negative ions and $c^-$ is their concentration as a function of the distance from the surface, $x$, as shown in Fig. 6.

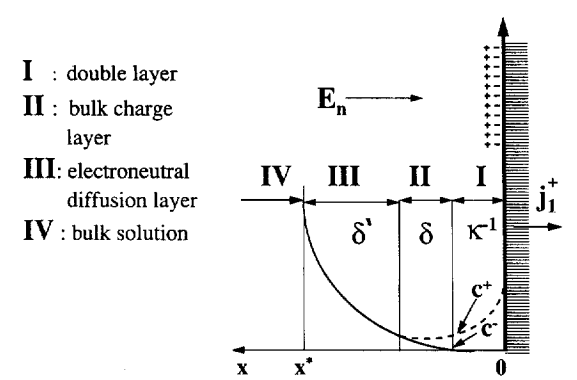


Fig. 6. Induction and location of a bulk charge layer formed by the selective permeation of counterions at flux $j_1^+$ through the ion exchanger surface as a result of the normal component of the electric field.

Upon integration, Eq. (21) yields the following expression for the concentration of the negative ions as [25,27]

$$c^-(x) = c_o e^{-\frac{e}{kT}[\psi(x) - \psi(x^*)]} \qquad (22)$$

where, $x^*$, as shown in Fig. 6, marks the outer boundary of the zone of concentration polarization where the concentration of the negative ions equals the bulk concentration, i.e. $c^- = c_o$.

Since the positive ions diffuse through the negatively charged ion-exchanger particle, the equation for the conservation of charge has to include the flux, $j_1^+$, so that we obtain

$$-D^+ \frac{dc^+(x)}{dx} - D^+ c^+(x) \frac{e}{kT} \frac{d\psi(x)}{dx} = j_1^+. \qquad (23)$$

The integrated form of Eq. (23) gives the following expression for $c^+$

$$c^+(x) = e^{-\frac{e}{kT}[\psi(x) - \psi(x^*)]} \times \left[ c_o - \frac{j_1^+}{D^+} \int_0^x e^{\frac{e}{kT}[\psi(x) - \psi(x^*)]} dx \right] \qquad (24)$$

which is different from Eq. (22) for $c^-$ because $c^+$ is a function also of $j_1^+$ [25,27].

In Fig. 6, $c^-$ and $c^+$ are plotted against $x$ according to Eq. (22) and Eq. (24) to show the bulk charge formed in the region between the double layer and the electroneutral diffusion layer, since electroneutrality is not obeyed in the diffuse part of the double layer. In very high fields, the bulk charge layer can be much thicker than the double layer or the diffusion layer, yet thinner in comparison to the particle. The induced bulk charge density, $\rho$, was expressed by Dukhin as

$$\rho(x) = e[c^+(\psi(x), j_1^+) - c^-(\psi(x))]. \qquad (25)$$

### 4.2. Tangential movement of ions in the diffuse layer

According to Dukhin, the tangential component of the field also contributes to induction of the bulk

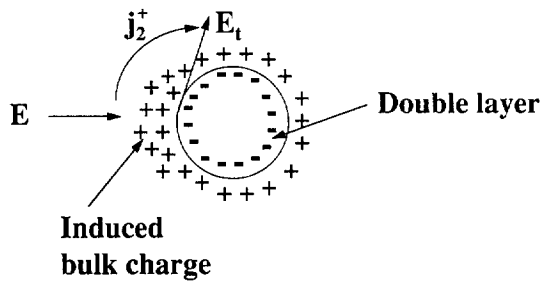


Fig. 7. Induction and location of a bulk charge layer formed by the tangential flow of the diffuse layer with flux $j_2^+$ at the surface of a curved ion exchanger as a result of the tangential component of the electric field.

charge according to a mechanism different from that discussed above. As illustrated in Fig. 7 for a charged spherical particle immersed in an electrolyte solution under the influence of the tangential component of the electric field, excess of counterions in the diffuse layer causes a net tangential flow of counterions, $j_2^+$, that acts as another sink for the counterions and enhances bulk charge formation.

### 4.3. Enhancement of EOF

A particular feature of Dukhin's model is the "electroosmotic whirlwind" around a conductive spherical particle with a polarized double layer in an electrolyte solution under the influence of strong electric field as a part of the mechanism for enhancement of EOF. It is shown schematically in Fig. 8

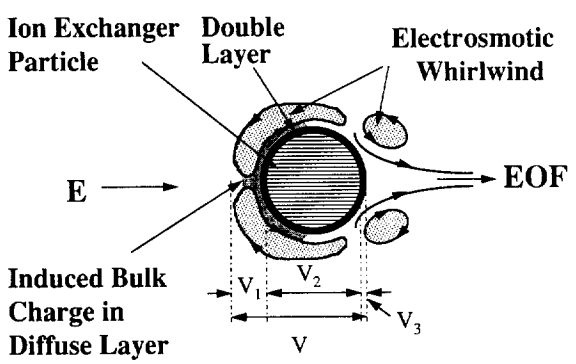


Fig. 8. Schematic illustration of the loci of the induced bulk charge layer and electrosmotic whirlwind around a highly conductive spherical ion exchanger particle immersed in an electrolyte solution of relatively low conductivity under the influence of high electric field.

where for the sake of illustration, the region where bulk charge is induced has been enlarged. In reality its thickness is much smaller than the particle diameter. It is seen that bulk charge is formed only upstream of the particle and the downstream side has only a thin double layer because the normal component of the electric field is in the direction away from the particle.

According to Dukhin and Mishchuk [25,27], the potential drop across the whole particle including the double layer and the bulk charge layer, $V$, is the sum of three contributions

$$V = V_1 + V_2 + V_3 \tag{26}$$

where, $V_1$, $V_2$ and $V_3$ are the respective potential drops across the bulk charge layer upstream, across the particle proper and across the thin double layer downstream as shown in Fig. 8.

Since the thickness of the double and the bulk charge layers is expected to be small in comparison to the particle diameter, the total potential drop, $V$, is given by

$$V = d_p E. \tag{27}$$

In order to evaluate the EOF under such conditions we make use of the two assumptions made earlier. The first assumption is that the particle conductivity is high enough so that the potential drop across the particle is a small part of the total potential drop, that can be expressed as

$$\sigma_p \gg \sigma_b\left(\frac{d_p}{\delta}\right) \tag{28}$$

where, $\sigma_p$ and $\sigma_b$ are the conductivities of the particle and electrolyte medium and $\delta$ is the thickness of the bulk charge layer. As a consequence of Eq. (28), the potential drop across the particle, $V_2$, is very small as compared to the total potential drop $V$.

$$V_2 < V. \tag{29}$$

The second assumption is that the electric field strength is so high that the potential drop across the double layer on the downstream side of the particle is small as compared to the total potential drop

$$V_3 = \zeta_p < V. \tag{30}$$

Combining Eqs. (26)–(30), we obtain that

$$V_1 \approx V = d_p E. \quad (31)$$

Eq. (31) implies that the total potential drop occurs across the bulk charge layer.

Let us introduce an apparent zeta potential, $\zeta_p^{\dagger}$, to express the potential drop across the bulk charge layer, $V_1$, so that

$$\zeta_p^{\dagger} = V_1 = d_p E. \quad (32)$$

Assuming that the potential drop, $V_1$, is uniform over the particle, i.e. the bulk charge layer is thin in comparison to the particle diameter, the EOF velocity can be expressed as

$$u = \left(\frac{\varepsilon\varepsilon_o E}{\eta}\right)(d_p E) = \left(\frac{\varepsilon\varepsilon_o E}{\eta}\right)(\zeta_p^{\dagger}). \quad (33)$$

Since the bulk charge is induced by an excess of counterions, the EOF velocity as predicted by this theory and given by Eq. (33) has the same direction as that would be observed at low electric field strengths when this effect is absent [25,27].

The extension of the Dukhin's model for the packed beds that are used in CEC can be done along similar lines as earlier. However, since the apparent zeta potential, $\zeta_p^{\dagger}$, under these conditions would be much larger than the zeta potential of the tube wall, the wall effect would also be very small resulting in a flat flow profile with the average EOF velocity given by

$$< u > = u = \left(\frac{\varepsilon\varepsilon_o E}{\eta}\right)(\zeta_p^{\dagger})\left(\frac{\sigma^*}{\sigma_b}\right). \quad (34)$$

According to Dukhin's model, enhancement of EOF in CEC would take place only when the conductivity of the column packing is higher than that of the stationary phases employed presently. The enhancement of EOF is favored by an increase in both the conductivity and size of the particles. As illustrated in Fig. 9 for fixed conductivity of the bulk electrolyte, under any given set of operating conditions a certain minimum particle conductivity is required to bring about a non-linear dependence of the EOF velocity on the electric field. However, upon increasing the particle conductivity at some point, saturation occurs and further increase does not produce any enhancement in the EOF velocity. The effect of the particle size on the enhancement of EOF is illustrated in Fig. 10, which shows that the formation of the bulk charge and the onset of "electrosmosis of second kind" occurs with large particles in an

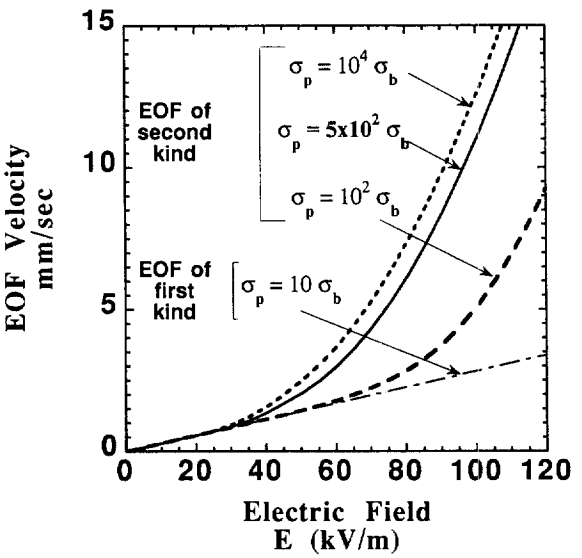


Fig. 9. Plots of the average EOF velocity versus the electric field strength according to Eq. (34) with the conductivity ratio of the packing particle and the bulk electrolyte as the parameter. Conditions; $d_p = 5$ μm, $\delta = 500$ Å; $\zeta_w = \zeta_p = 100$ mV, $\varepsilon = 80$; $\varepsilon_o = 8.85 \cdot 10^{-12}$ C V$^{-1}$ m$^{-1}$ and $\eta = 10^{-3}$ kg s$^{-1}$ m$^{-1}$.

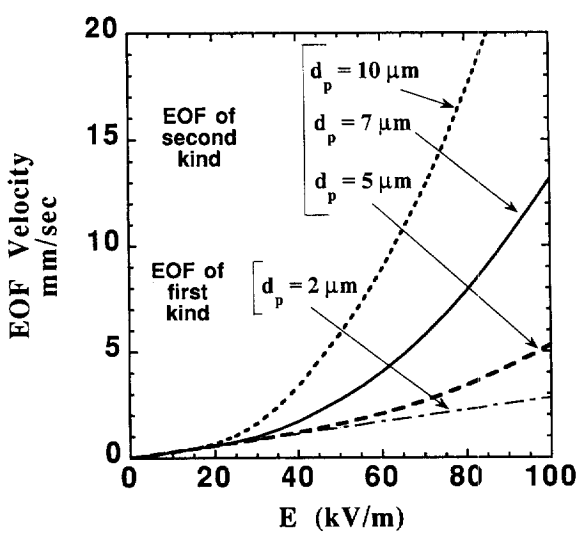


Fig. 10. Plots of the average EOF velocity versus the electrical field strength according to Eq. (34) with the particle diameter as the parameter. Conditions; $\sigma_p/\sigma_b = 5 \cdot 10^2$, $\delta = 500$ Å; $\zeta_w = \zeta_p = 100$ mV, $\varepsilon = 80$; $\varepsilon_o = 8.85 \cdot 10^{-12}$ C V$^{-1}$ m$^{-1}$ and $\eta = 10^{-3}$ kg s$^{-1}$ m$^{-1}$.

electric field that is much weaker than that required with smaller particles.

## 5. Conclusions

A solid theoretical basis for the flow field of EOF in porous media has yet to be established. The two, rather greatly simplified approaches reviewed above represent, to our best knowledge, the only theoretical framework available as a starting point for further theoretical developments and experimental design as well. The combination of the Smoluchowskian theory with the capillary bundle model for treating EOF in packed capillaries is beguilingly simple. Yet, it has not been confirmed experimentally as demonstrated by the present controversy about the effect of the particle size on the magnitude of EOF. In view of Overbeek's model EOF should not be dependent on the particle diameter of the packing as long as the double layer thickness is less than a tenth of the radius. It shall require carefully designed experiments to test the validity of the theoretical predictions presented above. If "electrosmosis of the second kind" could be brought about in electrochromatographic systems of practical significance, it would greatly facilitate rapid separations and the use of long columns that allow the generation of a large number of theoretical plates. We assumed so far that the dependence of the plate height in CEC on the EOF velocity is subject to the van Deemter or Knox equation, but this requires further experimental studies and validation. Some findings would suggest that these equations have to be corrected in order to take into account the reduced band spreading due to the interparticular electrosmotic flow field in CEC and the enhanced intraparticular mass transfer.

## 6. Symbols and abbreviations

| | |
|---|---|
| $c^+$ | Concentration of the positive ions as a function of distance from the surface |
| $c^-$ | Concentration of the negative ions as a function of distance from the surface |
| $c_o$ | Bulk concentration of the ions in the electrolyte |
| $d_p$ | Particle diameter of the column packing |
| $D^+$ | Diffusivity of the positive ions in the bulk electrolyte |
| $D^-$ | Diffusivity of the negative ions in the bulk electrolyte |
| $E$ | Applied electric field in the axial direction |
| $F_d$ | Net drag force acting on an annular element |
| $F_v$ | Net viscous force acting on an annular element |
| $I_0$ | Bessel's function of the zeroth order |
| $I_1$ | Bessel's function of the first order |
| $j$ | Current flowing through the packed column in CEC |
| $j_1^+$ | Flux of counterions through a packing particle |
| $j_2^+$ | Flux of counterions tangential to the packing particle |
| $k$ | Boltzmann constant |
| $r$ | Coordinate specifying distance from the center of the packed column |
| $R$ | Inner radius of the capillary |
| $T$ | Absolute temperature of the electrolyte |
| $u_p$ | EOF velocity at the particle surface |
| $u_r$ | Local EOF velocity at the particle surface in the packed bed |
| $u_w$ | EOF velocity at the capillary wall |
| $u_{rw}$ | Local EOF velocity generated in a capillary packed with neutral particles by the charged wall |
| $V$ | Total potential drop across the particle as well as the double and bulk charge layers |
| $V_1$ | Potential drop across the bulk charge layer upstream |
| $V_2$ | Potential drop across the particle proper |
| $V_3$ | Potential drop across the double layer |
| $V_c$ | Total column volume |
| $V_{cf}$ | Volume of the interstitial space |
| $x$ | Coordinate specifying distance from the surface of the particle |
| $x^*$ | Distance of the outer boundary of the zone of concentration polarization from the particle surface |

*Greek letters*

| | |
|---|---|
| $\alpha$ | Dimensionless packing parameter |
| $\beta$ | Dimensionless packing parameter |
| $\delta$ | Thickness of the bulk charge layer |
| $\delta'$ | Thickness of the electroneutral diffusion layer |

| | |
|---|---|
| $\varepsilon_c$ | Total porosity of the column |
| $\varepsilon$ | Dielectric constant of the medium |
| $\varepsilon_o$ | Permittivity of the vaccum |
| $\kappa$ | Reciprocal of thickness of the double layer |
| $\eta$ | Viscosity of the bulk electrolyte |
| $\rho$ | Induced bulk charge density |
| $\sigma^*$ | Conductivity of the packed column with the electrolyte |
| $\sigma_b$ | Conductivity of the electrolyte |
| $\sigma_p$ | Conductivity of the ion-exchanger packing without electrolyte |
| $\psi$ | Electrical potential as a function of the distance from the particle surface |
| $\zeta_p$ | Zeta potential at the particle surface |
| $\zeta_p^\dagger$ | Apparent zeta potential at the particle surface |
| $\zeta_w$ | Zeta potential at the capillary wall |

*Acronyms*

| | |
|---|---|
| CEC | Capillary electrochromatography |
| CZE | Capillary zone electrophoresis |
| EOF | Electrosmotic flow |
| HPLC | High-performance liquid chromatography |

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