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Electroosmotic coupling in porous media, a new model based on a fractal upscaling procedure

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Abstract

Electrokinetic and electroosmotic couplings can play important roles in water and ions transport in charged porous media. Electroosmosis is the phenomena explaining the water movement in a porous medium subjected to an electrical field. In this work, a new model is obtained through a new up-scaling procedure, considering the porous medium as a bundle of tortuous capillaries of fractal nature. From the model, the expressions for the electroosmosis pressure coefficient, the relative electroosmosis pressure coefficient, the maximum back pressure, the maximum flow rate, the flow rate-applied back pressure relation and the product of the permeability and formation factor of porous media are also obtained. The sensitivity of the relative electroosmosis pressure coefficient is then analyzed and explained. The model predictions are then successfully compared with published datasets. Additionally, we deduce an expression for the relative streaming potential coefficient and then compare it with a previously published model and experimental data from a dolomite rock sample. We find a good agreement between those models and experimental

data, opening up new perspectives to model electroosmotic phenomena in porous media saturated with various fluids.

14 *Keywords:* Electroosmosis; Electrokinetics; Water saturation; Zeta
15 potential; Fractal; Porous media

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16 **1. Introduction**

17 Electroosmosis is one of the effects of electrokinetic phenomena that occur in porous media with surface charges when filled with one or more fluids containing charged particles. It arises due to the induced movement of a liquid by a voltage across a porous sample and is directly linked to an electrical double layer between the solid grain surface and the pore solution. Electroosmosis has been studied both experimentally and theoretically for a long time (e.g., Reuss, 1809; Quincke, 1861; Smoluchowski, 1902; Nourbehecht, 1963; Lyklema, 1995). Electroosmotic flow is a critical phenomenon that is used in a variety of applications. For example, electroosmotic flow pumps have been used in different fields of microfluidics such as biological and chemical analysis (Good et al., 2006), liquid drug reagent injection/delivery (e.g., Tsai & Sue, 2007; Wang et al., 2009), microelectronic chip cooling (e.g., Linan Jiang et al., 2002; Singhal et al., 2004) and microfluidic devices (e.g., Hu & Li, 2007; Bruus, 2008; Kirby, 2010). Solutes and nonaqueous phase liquids/dense nonaqueous phase liquids can be removed by an electroosmotic technique in the vadose zone for remediation purposes (e.g., Bruell et al., 1992; Wise & Tran, 1994; Han et al., 2004; Reddy et al., 1997). Additionally, electroosmosis has great potential for the dewatering of earth masonry structures (e.g., Casagrande, 1983; Lockhart & Hart, 1988; Larue et al., 2006) or drying moisture ingress in existing buildings, stone and earth masonry structures (e.g., Lockhart & Hart, 1988; Ottosen & Rørig-Dalgaard, 2006; Bertolini et al., 2009).

39 Many studies on electroosmosis flow reported in the literature use cylindrical capillaries or microchannels between two parallel plates (e.g., Rice & Whitehead, 1965; Levine et al., 1975; Olivares et al., 1980; Ohshima & Kondo, 1990; Mohiuddin Mala et al., 1997; Vennela et al., 2011). In

porous media, electroosmotic flow has been presented using capillary bundle models with different capillary geometry such as rectangular, cylindrical and annular geometries (e.g., Wu & Papadopoulos, 2000; Pascal et al., 2012). Bandopadhyay et al. (2013) introduced the parameter of the electro-permeability that relates the flow rate with the applied voltage in porous media. Based on the electroosmotic flow in a single capillary, models for the height difference between the U-tube experiment caused by electroosmosis in a fully saturated porous medium were presented (e.g., Paillat et al., 2000; Liang et al., 2015). For characterization of electroosmotic micropumps fabricated by packing non-porous silica particles, a bundle of capillary tubes model was applied (e.g., Zeng et al., 2001; Yao & Santiago, 2003). Besides capillary tubes models, other approaches based on volume-averaging upscaling can be also applied to calculate the electrokinetic coupling in porous media (e.g., Pride, 1994; Revil & Linde, 2006; Revil et al., 2007).

It has been shown that natural porous media have fractal properties. Their pore space is statistically self-similar over several length scales (among many others, see Mandelbrot, 1982; Katz & Thompson, 1985; Yu & Cheng, 2002). Theory on the fractal nature of porous media has attracted much attention in different areas (e.g., Mandelbrot, 1982; Feder & Aharony, 1989). Therefore, models based on the fractal theory have been applied to study phenomena in both fully and partially saturated porous media (e.g., Cai et al., 2012a,b; Liang et al., 2014; Guarracino & Jougnot, 2018; Soldi et al., 2019; Thanh et al., 2018, 2019). However, to the best of our knowledge, the fractal theory has not yet been used to study electroosmosis in a porous medium under water saturated and partially saturated conditions.

In this work, we apply fractal theory in porous media to obtain a mechanistic analytical model to describe electroosmotic flow in porous media using a capillary tube model. From the derived model, the expressions for the electroosmotic pressure coefficient, the relative electroosmosis pressure coefficient, the maximum back pressure, the maximum flow rate, the flow rate-applied back pressure relation and the product of the formation factor and permeability of porous media are also obtained. To validate the model, the sensitivity of the relative electroosmosis pressure coefficient K_E^r to irreducible water saturation S_{irr} , ratio of the minimum pore radius to the maximum pore radius α and fractal dimension for pore space D_f is analyzed and explained. The model is then compared with published results in both

cases of full saturation and partial saturation. Additionally, the expression K_S^r is also deduced from K_E^r . From that, the change of the relative streaming potential coefficient K_S^r with the water saturation is predicted and compared with another model and with experimental data for a dolomite rock sample available in literature.

2. Theoretical background of electroosmosis

2.1. Theory of electroosmosis

Porous media are constituted by minerals (e.g., silicates, oxides, carbonates) or other materials (e.g., polymers, biological materials) that are generally electrically charged due to isomorphous substitutions (e.g., Hunter, 1981;

Figure 1: (a) Sketch of the electrical double layer at the surface of a mineral in contact with water. Comparison between the Debye-Hu"ckel (DH) approximation (plain line, Eq. (13)) and the Poisson-Boltzman equation (dashed line) to compute (b) the electrical potential distribution and (c) the ionic species relative concentration distribution in a capillary ($R = 0.25 \mu\text{m}$) containing a NaCl electrolyte with 10^{-4} mol/L (i.e., $\lambda = 0.0304 \mu\text{m}$). Note that the dashed and plain lines are perfectly superimposed, validating the use of Eq. (13).

Figure 2: Electroosmosis flow in a capillary tube.

89 Jacob & Subirm, 2006) as shown in Fig. 1. The pore fluid nearby solid 90 solution interface contains an excess of charges (counter-ions) to insure the 91 electro-neutrality of the entire system. These counter-ions are often cations 92 and surface charges are often negatively charged in environmental conditions. 93 Note that the surface charges strongly depend on the pH and that the sign 94 can change at low pH. The value at which the sign changes is called the point 95 of zero charge (e.g., Hunter, 1981; Leroy & Revil, 2004). This gives rise to 96 the charge distribution known as the electrical double layer (EDL) as shown 97 in Fig. 1a. The EDL is composed of a Stern layer, where counter-ions are 98 adsorbed onto the solid surface and are immobile, and a diffuse layer that 99 contains mobile counter-ions and co-ions. In the diffuse layer, the distribu100 tion of ions and electric potential are governed by the Poisson-Boltzman (PB) 101 equation in quasistatic conditions. The solution to the linear PB equation 102 for a cylinder is well-known and the electric potential decays over distance 103 from the charged surface as displayed in Fig. 1b using the code provided by 104 Leroy & Mainault (2018). Further away from the solid-solution is the bulk 105 electrolyte, free from surface charge influence, it contains an equal number 106 of cations and anions and is therefore electrically neutral (Fig. 1c). The 107 shear plane or the slipping plane is the closest place to the solid in which 108 water flow occurs and the electrical potential at this plane is called the zeta 109 potential (ζ). The zeta potential depends on parameters including mineral 110 composition of porous media, ionic species that are present in the fluid, the 111 pH of the fluid, fluid electrical conductivity and temperature etc. (see Hunter 112 (1981); Davis et al. (1978); Jaafar et al. (2009) for more details). 113 Reuss (1809) carried out the

first experiment on electroosmosis by applying a DC voltage across a water saturated porous sample in a U-tube. When a DC voltage is applied across a capillary containing water, ions in the EDL are submitted to an electric force and move to the electrode of opposite

site polarity. That leads to the movement of the fluid near the solid surface as well as the bulk liquid due to viscous forces. The net motion of liquid is called electroosmotic flow (Fig. 2). The pressure necessary to counterbalance electroosmotic flow is defined as the electroosmotic pressure (e.g., Jacob & Subirm, 2006).

2.2. Governing equations

The electrokinetic coupling in a fluid saturated porous medium is described by two linear equations (e.g., Li et al., 1995; Pengra et al., 1999)

$$\mathbf{U}_e = -\sigma \nabla V - \Pi_{12} \nabla P. \quad (1)$$

$$\mathbf{U}^f = -\Pi_{21} \nabla V - \frac{k}{\eta} \nabla P, \quad (2)$$

where $\mathbf{U}_e$ and $\mathbf{U}^f$ are the electric current density (A m^{-2}) and Darcy flux (m s^{-1}), V is the electrical potential (V), P is the pressure that drives the flow, σ and k are the electrical conductivity (S m^{-1}) and permeability (m^2) of the porous medium, η is the dynamic viscosity of the fluid, the off-diagonal coefficients (Π_{12} and Π_{21}) are the electrokinetic coupling coefficients. In the

steady state, those coupling coefficients must satisfy the reciprocal relation of Onsager: $\Pi_{12} = \Pi_{21} = \Pi$.

The streaming potential coefficient is defined when the electric current density $\mathbf{U}_e$ is zero (e.g., Li et al., 1995; Wang et al., 2016), leading to

$$K_S = \frac{\Delta V}{\Delta P} = -\frac{\Pi}{\sigma}. \quad (3)$$

Note that another formulation in which streaming potential coefficient for saturated porous media is described through the effective excess charge density $\hat{Q}_v$ (C/m^3) dragged by the flow of the pore water was proposed by (e.g., Revil & Leroy, 2004; Revil & Linde, 2006)

$$K_S = -\frac{\hat{Q}_v k}{\sigma \eta}. \quad (4)$$

138 The electroosmotic pressure coefficient is defined when the Darcy flux
 139 $\mathbf{U}_f$ is zero (e.g., Li et al., 1995; Wang et al., 2016), leading to

$$K_E = \frac{\Delta P}{\Delta V} = -\frac{\Pi \eta}{k}. \quad (5)$$

Figure 3: Sketch of the considered conceptual representative elementary volume (REV): Parallel and tortuous capillary tubes with radii following a fractal distribution.

140 By the volume averaging approach, Pride (1994) obtained the steady
 state 141 coupling coefficient under a thin electrical double layer
 assumption as

$$\Pi = \frac{\phi}{\tau} \frac{\epsilon_r \epsilon_0 \zeta}{\eta} = \frac{\epsilon_r \epsilon_0 \zeta}{F \eta}, \quad (6)$$

142 where ϵ_r is the relative permittivity of the fluid, ϵ_0 is the dielectric per 143 mittivity
 in vacuum, ϕ , τ and F are the porosity, hydraulic tortuosity and

144 formation factor of porous media, respectively. Note that the link $\phi F = \tau$
 145 has been used in Eq. (6) (e.g., Wyllie & Rose, 1950; Ghanbarian et al., 2013)
 146

147 Substituting Eq. (6) into Eq. (5), one obtains

$$K_E = -\frac{\epsilon_r \epsilon_0 \zeta}{F k}. \quad (7)$$

148 In this work, we will obtain the analytical models for K_E as well as other
 149 quantities based on a fractal upscaling approach instead of the volume
 aver 150 aging approach for partially saturated porous media.

151 3. Model development

152 3.1. Electrical potential distribution at pore scale

153 Consider binary symetric 1:1 electrolytes (e.g., NaCl) of bulk ionic con-154
centration C^0 (mol/m³) with an electrical potential $\psi(r)$ (V) at a distance 155 r
from the axis. If the excess charge density at this point is $\rho(r)$ (C m⁻³), 156 then the
Poisson equation is given by (e.g., Rice & Whitehead, 1965; Gierst, 157 1966)

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi(r)}{dr} \right) = -\frac{\rho(r)}{\epsilon_r \epsilon_0}, \quad (8)$$

158 From the Boltzmann equation, the following is obtained

$$\rho(r) = NeC^0 \left[e^{-\frac{e\psi(r)}{k_b T}} - e^{\frac{e\psi(r)}{k_b T}} \right] = 2NeC^0 \sinh \frac{e\psi(r)}{k_b T} \quad (9)$$

159 where k_b is the Boltzmann's constant, T is temperature (in K), N is the 160
Avogadro number and e is the elementary charge.

161 If $\left| \frac{e\psi(r)}{k_b T} \right| \ll 1$ that is called the Debye-Hu"ckel approximation (e.g.,
Pride,

162 1994; Hunter, 1981; Jougnot et al., 2019), $\sinh \frac{e\psi(r)}{k_b T} \approx \frac{e\psi(r)}{k_b T}$. The
Poisson₁₆₃ Boltzmann equation
now becomes

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi(r)}{dr} \right) = -\frac{2Ne^2 C^0}{\epsilon_0 \epsilon_r k_b T} \psi(r) \quad (10)$$

164 OR

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi(r)}{dr} \right) = -\frac{\psi(r)}{\lambda^2} \quad (11)$$

165 where $\lambda = \sqrt{\frac{\epsilon_0 \epsilon_r k_b T}{2Ne^2 C^0}}$ is defined as the Debye length (e.g., Israelachvili, 1992).

166 The boundary conditions of Eq. (11) to be satisfied for the cylindrical 167
capillary surface are (Rice & Whitehead, 1965):

$$\psi(r) = \begin{cases} \psi(R) = \zeta \\ \frac{d\psi(r)}{dr} \Big|_{r=0} = 0 \end{cases} \quad (12)$$

168 Under the boundary conditions given by Eq. (12), the analytical solution
of 169 $\psi(r)$ and $\rho(r)$ are obtained as (Rice & Whitehead, 1965)

$$\psi(r) = \zeta \frac{I_o\left(\frac{r}{\lambda}\right)}{I_o\left(\frac{R}{\lambda}\right)} \quad (13)$$

170 and

$$\rho(r) = -\frac{\epsilon_0 \epsilon \zeta}{\lambda^2} \frac{I_0\left(\frac{r}{\lambda}\right)}{I_0\left(\frac{R}{\lambda}\right)} \quad (14)$$

171 where I_0 is the zero-order modified Bessel function of the first kind. Figure 1
172 compares the potential and concentrations of ions in the EDL calculated
from 173 Eq. (13) and the exact Poisson-Boltzmann solution (see Leroy &
Maineult 174 (2018) for more details). It shows that Eq. (13) is a correct
approximation 175 for the Poisson-Boltzmann true solution.

176 3.2. Velocity distribution at pore scale

177 Under application of an electric field E and a fluid pressure difference ΔP
178 across a tortuous capillary of radius R , the fluid flow is the sum of a
Poiseuille 179 flow generated by ΔP and an electroosmotic flow generated
by E acting on 180 the charge density in the EDL given by Eq. (14).
Consequently, the velocity 181 profile $v(r)$ in a cylindrical capillary is given
as (Rice & Whitehead, 1965)

$$v(r) = \frac{1}{4\eta}(R^2 - r^2)\frac{\Delta P}{L_\tau} + \frac{\epsilon_r \epsilon_0 \zeta E}{\eta} \left[1 - \frac{I_0(r/\lambda)}{I_0(R/\lambda)} \right], \quad (15)$$

182 where L_τ is the length of tortuous capillaries.

183 Because the electric field E is related to the applied voltage across the 184
porous medium ΔV by $E = \Delta V/L$ (L is the length of the porous medium as 185
shown in Fig. 3). Eq. (15) is rewritten as

$$v(r) = \frac{1}{4\eta}(R^2 - r^2)\frac{\Delta P}{L_\tau} + \frac{\epsilon_r \epsilon_0 \zeta}{\eta} \left[1 - \frac{I_0(r/\lambda)}{I_0(R/\lambda)} \right] \frac{\Delta V}{L}. \quad (16)$$

186 The volume flow rate in the capillary is

$$q(R) = \int_0^R v(r) 2\pi r dr = \frac{\pi R^4}{8\eta} \frac{\Delta P}{L_\tau} + \frac{\pi \epsilon_r \epsilon_0 \zeta R^2}{\eta} \left[1 - \frac{2\lambda I_1(R/\lambda)}{R I_0(R/\lambda)} \right] \frac{\Delta V}{L}, \quad (17)$$

187 where I_1 is the first-order modified Bessel functions of the first kind.

188 Figure 4 shows the variation of the nondimensional parameter of the sec¹⁸⁹
ond term in square brackets in Eq. (17) denoted by $C = 2\lambda I_1(R/\lambda)/(R I_0(R/\lambda))$
190 with R/λ . It is seen that when the pore size is much bigger than the Debye
191 length (hundred times), the term of $2\lambda I_1(R/\lambda)/(R I_0(R/\lambda))$ is much smaller
192 than the unity and can be ignored (see Rice & Whitehead (1965) for more

details). Under that condition called the thin EDL assumption, Eq. (17) becomes

$$q(R) = \frac{\pi R^4 \Delta P}{8\eta L_\tau} + \frac{\pi \epsilon_r \epsilon_0 \zeta R^2}{\eta} \frac{\Delta V}{L}. \quad (18)$$

In geological media and under most environmental conditions (i.e., ground-water for human consumption or subsurface reservoirs), ionic strengths (i.e.,

Figure 4: The variation of the unitless coefficient $C = 2\lambda I_1(R/\lambda)/(R I_0(R/\lambda))$ with the unitless ratio of the considered pore size and the Debye length (R/λ)

a proxy for ionic concentration) in potable water typically vary between 10^{-3} and 10^{-2} mol/L (Jougnot et al., 2019). Reservoirs can be saturated with brine having much higher ionic concentrations depending on the formation. Therefore, the Debye length is typically less than 10 nm at 25°C (Israelachvili, 1992). It suggests that the minimum pore radius of porous materials that is applicable for thin EDL under the environmental conditions is around $100 \times 10 \text{ nm} = 1 \mu\text{m}$. In addition, typical characteristic radius of pore in geological media is tens of micrometer (e.g., Hu et al., 2017). Therefore, a thin EDL assumption (no EDL overlap) is normally satisfied in most natural systems (see Jougnot et al. (2019) for more details). It is noted that the thin EDL assumption does not work for clay rocks and low permeability sediments where the pore size is on the order of 10 nm. Therefore, one needs to take into account the term of $C = 2\lambda I_1(R/\lambda)/(R I_0(R/\lambda))$ in Eq. (17). It is therefore a limitation to the proposed model.

211 3.3. Fractal based up-scaling

212 Porous media can be conceptualized as a bundle of tortuous capillary 213 tubes following a fractal pore-size distribution (e.g., Yu & Cheng, 2002; Liang 214 et al., 2014) (see Fig. 3). The fractal approach is a simple and elegant way to 215 upscale microscopic properties to macroscopic properties by assuming that 216 the pore size distribution follows the fractal scaling law

$$N(\geq R) = \left(\frac{R_{max}}{R}\right)^{D_f}, \quad (19)$$

217 where N is the number of capillaries with radius greater than R , R_{max} is the 218 maximum radius, D_f is the fractal dimension for pore space, $0 < D_f < 2$ 219 in two-dimensional space and $0 < D_f < 3$ in three dimensional space (Yu & 220 Cheng, 2002; Liang et al., 2014).

221 From Eq. (19), the following is obtained

$$-dN = D_f R_{max}^{D_f} R^{-D_f-1} dR, \quad (20)$$

222 where $-dN$ is the number of capillaries with radius ranging from R to $R+dR$. 223 The minus (-) in Eq. (20) implies that the number of pores decreases with 224 the increase of pore size. The total number of capillaries with radius ranging 225 from R_{min} (the minimum radius) to R_{max} (the maximum radius) is given by

$$N_{total}(\geq R_{min}) = \left(\frac{R_{max}}{R_{min}}\right)^{D_f}. \quad (21)$$

226 From Eq. (20) and Eq. (21), the following is obtained

$$-\frac{dN}{N_{total}} = D_f R_{min}^{D_f} R^{-D_f-1} dR = f(R) dR, \quad (22)$$

227 in which $f(R) = D_f R_{min}^{D_f} R^{-D_f-1}$ is the probability density function. Accord-
228 ing to the statistical theory, the probability density function needs to meet
229 the following condition

$$\int_{R_{min}}^{R_{max}} f(R) dR = 1 - \left(\frac{R_{min}}{R_{max}}\right)^{D_f} = 1 \quad (23)$$

230 OR

$$\left(\frac{R_{min}}{R_{max}}\right)^{D_f} \approx 0 \quad (24)$$

Eq. (24) is approximately valid for $R_{min}/R_{max} \approx 10^{-2}$ or $< 10^{-2}$ (Yu & Cheng, 2002; Liang et al., 2014). That condition generally holds in porous media. The fractal dimension D_f is linked to the porosity of porous media and the ratio of the minimum capillary radius to the maximum capillary radius ($\alpha = R_{min}/R_{max}$) by following equation (e.g., Yu et al., 2001; Yu & Cheng, 2002)

$$D_f = 2 - \frac{\ln \phi}{\ln \alpha} \quad (25)$$

3.4. REV scale

To obtain the volume flow rate at the macroscale, a representative elementary volume (REV) as a cube with a length L is considered. As presented in the previous section, the porous medium exhibits a fractal pore size distribution with radii varying from R_{min} to R_{max} . We consider the REV under varying saturation conditions. The effective saturation is defined by

$$S_e = \frac{S_w - S_{irr}}{1 - S_{irr}}, \quad (26)$$

where S_w is the water saturation and S_{irr} is irreducible water saturation. We assume that the REV is initially fully saturated and then drained when submitted to a pressure head h (m). For a capillary tube, the pore radius R_h (m) that is drained at a given pressure head h can be calculated by (Jurin, 1719)

$$h = \frac{2T_s \cos \beta}{\rho_w g R_h}, \quad (27)$$

where T_s (N/m) is the surface tension of the fluid and β is the contact angle. A capillary becomes fully desaturated under the pressure head h if R is greater than the radius R_h given by Eq. (27). Therefore, the capillaries with radii R between R_{min} and R_h will be fully saturated under the pressure head

h .

For porous media containing only large and regular pores, the irreducible water saturation can often be neglected. For porous media containing small pores, the irreducible water saturation can be pretty significant because water

remains trapped in the crevices or in micropores that are not occupied by air. This amount of water is taken into account in the model by setting irreducible water radius of capillaries R_{irr} . Consequently, the following assumptions are

made in this work: (1) for $R_{min} \leq R \leq R_{irr}$, the capillaries are occupied by water that is immobile at irreducible saturation due to insufficient driving force, so it does not contribute to fluid flow; (2) for $R_{irr} < R \leq R_h$, the capillaries are occupied by mobile water, so it contributes to the fluid flow; (3) for $R_h < R \leq R_{max}$, the capillaries are occupied by air, so it does not contribute to the fluid flow. In this work, film bound water adhering to the capillary walls of porous media with radius greater than R_{irr} is ignored. Therefore, the irreducible water saturation is defined as

$$S_{irr} = \frac{\int_{R_{min}}^{R_{irr}} \pi R^2 L_\tau (-dN)}{\int_{R_{min}}^{R_{max}} \pi R^2 L_\tau (-dN)} = \frac{R_{irr}^{2-D_f} - R_{min}^{2-D_f}}{R_{max}^{2-D_f} - R_{min}^{2-D_f}}. \quad (28)$$

The water saturation is determined as:

$$S_w = \frac{\int_{R_{min}}^{R_h} \pi R^2 L_\tau (-dN)}{\int_{R_{min}}^{R_{max}} \pi R^2 L_\tau (-dN)} = \frac{R_h^{2-D_f} - R_{min}^{2-D_f}}{R_{max}^{2-D_f} - R_{min}^{2-D_f}}. \quad (29)$$

Because only capillaries with radius between R_{min} and R_h are fully saturated under a pressure head h , the volumetric flow rate Q_{REV} through the REV is the sum of the flow rates over all capillaries with radius between R_{irr} and R_h and given by

$$Q_{REV} = \int_{R_{irr}}^{R_h} q(R) (-dN) \quad (30)$$

Combining Eq. (18), Eq. (20) and Eq. (30), the following is obtained

$$Q_{REV} = \frac{\pi R_{max}^{D_f}}{8\eta} \frac{D_f (R_h^{4-D_f} - R_{irr}^{4-D_f})}{(4-D_f)} \frac{\Delta P}{L_\tau} + \frac{\pi R_{max}^{D_f} \epsilon_r \epsilon_0 \zeta}{\eta} \frac{D_f (R_h^{2-D_f} - R_{irr}^{2-D_f})}{(2-D_f)} \frac{\Delta V}{L} \quad (31)$$

Additionally, from Eq. (28) and Eq. (29) one has

$$R_{irr} = R_{max} [\alpha^{2-D_f} + S_{irr} (1 - \alpha^{2-D_f})]^{\frac{1}{2-D_f}} \quad (32)$$

and

$$R_h = R_{max} [\alpha^{2-D_f} + S_w(1 - \alpha^{2-D_f})]^{\frac{1}{2-D_f}}, \quad (33)$$

where $\alpha = R_{min}/R_{max}$.

Combining Eq. (31), Eq. (32) and Eq. (33), the following is obtained

$$Q_{REV} = \frac{\pi R_{max}^4 D_f}{8\eta(4 - D_f)} \left\{ [\alpha^{2-D_f} + S_w(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\} \frac{\Delta P}{L_\tau} \\ + \frac{\pi R_{max}^2 \epsilon_r \epsilon_0 \zeta D_f}{\eta(2 - D_f)} S_w(1 - \alpha^{2-D_f})(S_w - S_{irr}) \frac{\Delta V}{L}. \quad (34)$$

The total flow rate Q through the porous medium is given by

$$Q = Q_{REV} \frac{A}{A_{REV}}, \quad (35)$$

where A and A_{REV} are the cross sectional areas of the porous medium and the REV, both are perpendicular to the flow direction.

The porosity is calculated by

$$\phi = \frac{V_{pore}}{V_{REV}} = \frac{\int_{R_{min}}^{R_{max}} L_\tau \pi R^2 (-dN)}{L A_{REV}} = \frac{\pi \tau D_f R_{max}^2 (1 - \alpha^{2-D_f})}{(2 - D_f) A_{REV}}, \quad (36)$$

where τ is the mean tortuosity of the porous medium defined by the relation $L_\tau = \tau L$.

The cross sectional area of the REV is therefore obtained as

$$A_{REV} = \frac{\pi \tau D_f R_{max}^2 (1 - \alpha^{2-D_f})}{(2 - D_f) \phi}. \quad (37)$$

Combining Eq. (34), Eq. (35) and Eq. (37), one obtains

$$Q = \frac{R_{max}^2 A (2 - D_f)}{8\eta \tau (4 - D_f)} \frac{\phi}{(1 - \alpha^{2-D_f})} \times \\ \left\{ [\alpha^{2-D_f} + S_w(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\} \frac{\Delta P}{L_\tau} \\ + \frac{\epsilon_r \epsilon_0 \zeta \phi A}{\eta \tau} (S_w - S_{irr}) \frac{\Delta V}{L} \quad (38)$$

Eq. (38) indicates that the total volumetric flow rate relates to the zeta potential, fluid properties (relative permittivity, viscosity), water saturation, irreducible water saturation as well as the microstructural parameters of porous media ($D_f, \phi, \alpha, r_{max}, \tau$). Eq. (38) predicts that when $S_w = S_{irr}$ ($S_e=0$) then $Q = 0$ (i.e., no water flow). When the porous medium is fully saturated $S_w = 1$ and the irreducible water saturation equals zero $S_{irr} = 0$, the total volumetric flow Q becomes

$$Q = \frac{R_{max}^2 A (2 - D_f)}{8\eta\tau} \frac{\phi}{(4 - D_f) (1 - \alpha^{2-D_f})} (1 - \alpha^{4-D_f}) \frac{\Delta P}{L\tau} + \frac{\epsilon_r \epsilon_0 \zeta \phi A \Delta V}{\eta\tau L} \quad (39)$$

Because $1 < D_f < 2$ and $2 < 4 - D_f < 3$, $\alpha^{4-D_f} < 1$ ($\alpha = R_{min}/R_{max} \leq 10^{-2}$ in porous media as previously reported). Using $1 - \alpha^{2-D_f} = 1 - \phi$ as shown by Eq. (25), Eq. (39) is rewritten as

$$Q = \frac{R_{max}^2 A (2 - D_f)}{8\eta\tau} \frac{\phi}{(4 - D_f) (1 - \phi)} \frac{\Delta P}{L\tau} + \frac{\epsilon_r \epsilon_0 \zeta \phi A \Delta V}{\eta\tau L} \quad (40)$$

Eq. (40) is exactly the same as that reported in Liang et al. (2015) under the thin EDL assumption and full saturation.

From Eq. (38), we will obtain the link between fluid pressure difference and flow rate as well as the electroosmotic pressure coefficient.

3.5. Relationship between the flow rate and back pressure difference

Under the condition of zero flow rate ($Q = 0$), the maximum back pressure generated across the porous medium is obtained as

$$\Delta P_m = - \frac{8\epsilon_r \epsilon_0 \zeta \Delta V \tau (1 - \phi) (4 - D_f)}{R_{max}^2 (2 - D_f)} \times \frac{S_w - S_{irr}}{\left\{ [\alpha^{2-D_f} + S_w (1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr} (1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\}} \quad (41)$$

Under the condition of zero back pressure difference ($\Delta P = 0$), the total flow rate is maximum as

$$Q_m = \frac{\epsilon_r \epsilon_0 \zeta A \phi}{\eta\tau} (S_w - S_{irr}) \frac{\Delta V}{L} \quad (42)$$

Combining Eq. (38), Eq. (41) and Eq. (42), the link between the pressure difference and the flow rate is given by

$$Q = Q_m \left[1 - \frac{\Delta P}{\Delta P_m} \right] \quad (43)$$

Eq. (43) is exactly the same as that obtained in Zeng et al. (2001) in which the porous medium was conceptualized as a bundle of parallel capillaries of the same radii at full saturation condition. Interestingly, Eq. (43) is obtained in this work for the fractal pore size distribution and for partially saturated porous media but the result is the same for the relationship between flow rate and pressure difference.

3.6. Electroosmotic pressure coefficient

The electroosmotic pressure coefficient K_E is defined by $\Delta P/\Delta V$, that means the K_E is a macroscopic variable (i.e., integrating over the entire bundle of capillaries) when the total flow rate Q in Eq. (38) equals zero (Li et al., 1995; Wang et al., 2016). Consequently, one has

$$K_E = \frac{\Delta P}{\Delta V} \Big|_{Q=0} = \frac{\Delta P_m}{\Delta V} \quad (44)$$

Using Eq. (41), Eq. (44) is rewritten as

$$K_E = - \frac{8\epsilon_r\epsilon_0\zeta\tau(1-\phi)(4-D_f)}{R_{max}^2(2-D_f)} \times \frac{S_w - S_{irr}}{\left\{ [\alpha^{2-D_f} + S_w(1-\alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr}(1-\alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\}}. \quad (45)$$

Eq. (45) is a general expression for the electroosmotic pressure coefficient

for partially saturated porous media. Eq. (45) indicates that the electroosmotic pressure coefficient is explicitly linked to ζ , microstructural parameters of porous media (D_f , ϕ , α , R_{max} , τ), water saturation and irreducible water saturation. Therefore, the model can indicate more mechanisms influencing the electroosmotic pressure coefficient than other published models (e.g., Eq. (7) deduced by the volume averaging approach).

In case of full saturation $S_w = 1$, Eq. (45) becomes

$$K_E^{sat} = - \frac{8\epsilon_r\epsilon_0\zeta\tau(1-\phi)(4-D_f)}{R_{max}^2(2-D_f)} \frac{1-S_{irr}}{\left\{1 - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}}. \quad (46)$$

328 The relative electroosmotic pressure coefficient K_E^r is defined as

$$\begin{aligned} K_E^r &= \frac{K_E}{K_E^{sat}} = \frac{S_w - S_{irr}}{1 - S_{irr}} \frac{\left\{1 - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}}{\left\{[\alpha^{2-D_f} + S_w(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}} \\ &= S_e \frac{\left\{1 - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}}{\left\{[\alpha^{2-D_f} + S_w(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}}. \end{aligned} \quad (47)$$

329 4. Results and discussion

330 4.1. Predictions of the model under partially saturated conditions

331 The values of α between 0.001 and 0.01 are used in this section for model 332
ing because those values are normally used in published works (Yu & Cheng, 333
2002; Liang et al., 2014; Thanh et al., 2019). The fractal dimension D_f is in 334 the
range between 1 and 2. For given porous media, D_f is determined via 335 Eq. (25)
with known values of α and porosity ϕ . Fig. 5 shows (a) the influ 336 ence of the
irreducible saturation on the change of the relative electroosmotic 337 pressure
coefficient K_E^r with the water saturation S_w ($S_{irr} = 0.02, 0.05$ and

338 0.1) for $\alpha = 0.01$ and $D_f = 1.8$; (b) influence of α on the variation of K_E^r

339 with S_w ($\alpha = 0.002, 0.005, 0.01$) for $S_{irr} = 0.05$ and $D_f = 1.8$ and (c) Influ 340 ence
of D_f on the variation of K_E^r with S_w ($D_f = 1.3, 1.5, 1.8$) for $\alpha = 0.01$ 341 and $S_{irr} =$
0.05. The results show that as the media desaturate, the relative 342
electroosmotic pressure coefficient K_E^r increases. The reason is that at lower
343 water saturation, only capillaries with smaller radii are occupied by
water. 344 Therefore, one needs larger pressure differences over porous
media to counter 345 balance with the flow rate generated by the same
applied voltage (such that 346 the total volumetric flow rate is zero). As a
result, K_E^r is larger for lower

347 water saturation. Additionally, Fig. 5 shows that the relative electroosmotic 348
 pressure coefficient is very sensitive to the fractal dimension D_f and the ratio 349
 α . It is noted that the D_f decreases with an increase of α at a given porosity 350 as
 indicated by Eq. (25). Fig. 5 also shows that the K_{E^r} decreases with the 351
 increase of the ratio α and decrease of D_f . That can be explained by the 352
 decrease of the total number of pores in the REV with the decrease of D_f .

Figure 5: Sensitivity analysis of the model: (a) Influence of the irreducible saturation on the variation of the K_{E^r} with the water saturation S_w ($S_{irr} = 0.02, 0.05$ and 0.1) for $\alpha = 0.01$ and $D_f = 1.8$; (b) Influence of α on the variation of K_{E^r} with S_w ($\alpha = 0.002, 0.005, 0.01$) for $S_{irr} = 0.05$ and $D_f = 1.8$; (c) Influence of D_f on the variation of K_{E^r} with S_w ($D_f = 1.3, 1.5, 1.8$) for $\alpha = 0.01$ and $S_{irr} = 0.05$.

Figure 6: The variation of the zeta potential with pore fluid salinity. The predicted values of the zeta potential for four samples of glass beads at 0.1 mol/L in Li et al. (1995) are shown by red squares. Experimental data from different sources reported by Thanh & Sprik (2015), Jaafar et al. (2009) and Vinogradov et al. (2010) are also presented.

Therefore, R_h becomes larger at the same water water saturation. Similarly, we need to apply a smaller pressure difference over the partially saturated REV to counter balance the flow rate generated by the same applied voltage. Consequently, K_E^r decreases with a decrease of D_f .

4.2. Comparison with experimental data in water saturated porous media

Even if the present model is developed based on the concept of capillary tubes, it possible to provide a relationship between capillary radius to grain size for the sake of medium characterization. Indeed, in non-consolidated granular materials, pore size are very difficult to obtain without perturbing the medium, while grain sizes and grain size distribution can be easily measured. Therefore, with the knowledge of the mean grain diameter d of a granular material, the maximum pore radius can be determined by (e.g., Liang et al., 2015)

$$R_{max} = \frac{d}{4} \left[\sqrt{\frac{\phi}{1-\phi}} + \sqrt{\frac{1}{1-\phi}} \right]. \quad (48)$$

Mean geometrical tortuosity of porous media is predicted from porosity (e.g., Cai et al., 2012a; Ghanbarian et al., 2013; Liang et al., 2015)

$$\tau = \frac{1}{2} \left[1 + \frac{1}{2} \sqrt{1-\phi} + \sqrt{1-\phi} \frac{\sqrt{(1/\sqrt{1-\phi} - 1)^2 + 1/4}}{1 - \sqrt{1-\phi}} \right] \quad (49)$$

Table 1: Input parameters of four samples of fused glass beads are taken from Li et al. (1995). Symbols of d , φ , K_E and α are symbols for the grain diameter, porosity, the electroosmotic pressure coefficient and ratio of minimum and maximum radius, respectively. The values of ζ are predicted from Eq. (45)

Number	d (μm)	φ (no units)	K_E (Pa/V)	α (no units)	ζ (mV)
1	50	0.10	4.94	0.01	-11
2	50	0.17	12.5	0.01	-48
3	100	0.19	1.9	0.01	-33
4	200	0.30	0.25	0.01	-29
mean					-30

We want to see if the model is able to predict the zeta potential using Eq. (46). Li et al. (1995) measured K_E for fused glass beads fully saturated by a 0.1 M NaCl electrolyte. Micro-structure parameters of the samples such as grain diameter d , porosity φ as well as the measured K_E are reported in Li et al. (1995) and re-shown in Table 1. At this electrolyte concentration, the Debye length λ is around 1 nm (Israelachvili, 1992). Of all samples, the minimum value of R_{max} corresponding to the sample 1 ($d=50 \mu\text{m}$ and $\varphi=0.1$) is predicted using Eq. (48) to be $17 \mu\text{m}$. Hence, R_{min} corresponding

to the sample 1 is obtained using $R_{min} = \alpha R_{max} = 0.01 R_{max} = 170 \text{ nm}$. Consequently, the Debye length is much smaller than R_{min} and Eq. (46) is applicable for experimental data reported by Li et al. (1995).

The value of α is taken as 0.01 because that is a normally used value for grain materials (e.g., Thanh et al., 2018, 2019). The value of S_{irr} is reasonably taken as 0 for large grain materials (e.g., Jougnot et al., 2012). From the known values of porosity φ and α of samples (see Table 1), D_f is obtained by Eq. (25). From Eq. (46), the zeta potential is obtained with the knowledge of α , D_f , τ , φ , R_{max} and S_{irr} . The predicted values are presented in Table 1. It is seen that the predicted values (see red squares at 0.1 mol/L in Fig. 6) are in good agreement with published experimental data (Jaafar et al., 2009; Vinogradov et al., 2010; Thanh & Sprik, 2015).

The zeta potential is dependent on the electrical conductivity of the fluid. The electroosmotic pressure coefficient K_E^{sat} varies with the electrolyte electrical conductivity σ_w . Fig. 7 shows the variation of the electroosmotic pressure coefficient with fluid electrical conductivity experimentally obtained by

Figure 7: Variation of the electroosmotic pressure coefficient K_E^{sat} at saturated condition with electrolyte electrical conductivity for two consolidated samples of glass beads: (a) for the sample of 100 μm glass beads and (b) for the sample of 200 μm glass beads shown in Table 1).

Pengra et al. (1999) for two samples of glass beads ($d=100\text{ }\mu\text{m}$ and $200\text{ }\mu\text{m}$, respectively) saturated by a NaCl electrolyte (see diamond symbols). There are few proposed expressions for the relationship between the zeta potential and electrolyte concentration available in the literature (e.g., Pride & Morgan, 1991; Jaafar et al., 2009; Vinogradov et al., 2010). One is given by $\zeta = a + b\log_{10}(C_f)$ with $a = -6.43\text{ mV}$, $b = 20.85\text{ mV}$ as shown by Jaafar et al. (2009), for example. Electrical conductivity of the NaCl electrolyte is linked to the electrolyte concentration by the relation $\sigma_w = 10C_f$ for the ranges $10^{-6}\text{ M} < C_f < 1\text{ M}$ and $15^\circ\text{C} < T < 25^\circ\text{C}$ (Sen & Goode, 1992). Therefore, the relation $\zeta = -6.43 + 20.85\log_{10}(0.1\sigma_w)$ (mV) is obtained. Similarly, we obtain $R_{min} = 400\text{ nm}$ for two samples and maximum value of $\lambda = 1.36\text{ nm}$ for the considered range of electrolyte concentration by Pengra et al. (1999) (from 0.05 mol/L to 0.65 mol/L). Therefore, the thin EDL assumption is satisfied. Applying the same approach as we did previously, the variation of the electroosmotic pressure coefficient K_E^{sat} with electrical conductivity σ_w is predicted as shown in Fig. 7 by square symbols. One can see that the model prediction is also in

good match with data measured by Pengra et al. (1999) (diamond symbols) even there is a large difference between the model prediction and measured data for smaller glass beads at high electrical conductivity. The reason may be that Jaafar et al. (2009) obtained:

$$\zeta = a + b \log_{10}(C_f) \quad (50)$$

by fitting experimental data for quartz, silica, glass and St. Bees in NaCl brine with big data scattering. As shown in Fig. 3 of Jaafar et al. (2009), the difference in ζ can reach 65% at $C_f = 10^{-2}$ mol/L. Therefore, the $\zeta - C_f$ relation may not work well for a single silica-based sample in a large range of electrolyte concentration. As a matter of fact, Cherubini et al. (2018) show that, for data on carbonate materials, the best fit they obtain is rather $a = -6.97$ mV and $b = 9.13$ mV, indicating that this relationship is largely mineral dependent.

Figure 8 shows the variation of ΔP_m with an applied voltage for the 10 μm sand pack saturated with 10^{-3} M NaCl. The symbols are deduced from Luong & Sprik (2013) (their Fig. 10) using the relation $\Delta P_m = \rho g \Delta h_m$ (Δh_m is the maximum height difference obtained from Luong & Sprik (2013), $\rho = 1000$ kg/m³ is the water density and $g = 10$ m/s² is the acceleration due to

Table 2: Parameters taken from Wang et al. (2015) for 10 sandstone samples in which ϕ , k , ζ stand for porosity, permeability, the zeta potential. The electroosmotic pressure coefficient K_E^{exp} is deduced by comparison between the similarity of porosity, permeability, depth of samples between Wang et al. (2015) and Wang et al. (2016). K_E^{theo} is predicted from the model.

Sample	ϕ (no units)	k (10 ⁻¹⁵ m ²)	ζ (V)	K_{Exp} (Pa/V)	K_{Theo} (Pa/V)
D1	30.6	1028	-0.0486	0.42	0.44
D2	30.2	1435	-0.0571	0.47	0.35
D3	30.9	1307	-0.0410	0.40	0.31
D4	32.1	1152	-0.0609	0.40	0.61
D5	29.8	456	-0.0727	0.52	1.30
D6	31.0	978	-0.0462	0.51	0.46
D7	29.4	594	-0.0627	0.49	0.82
D8	31.0	2785	-0.1448	0.52	0.51
D9	29.3	1491	-0.0765	0.43	0.40

D10 31.5 3241 -0.0639 0.51 0.21

425 gravity). At the saturated condition, Eq. (41) becomes

$$\Delta P_m = - \frac{8\epsilon_r\epsilon_0\zeta\Delta V\tau(1-\phi)(4-D_f)}{R_{max}^2(2-D_f)} \times \frac{1-S_{irr}}{\left\{1 - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}} \quad (51)$$

426 The solid line is predicted from Eq. (51) in the same manner as
mentioned 427 above with $\phi = 0.38$, $D_f = 0.01$, $d = 10 \mu\text{m}$, $\alpha = 0.01$ and the mean
value

428 of $\zeta = -13 \text{ mV}$ over six granular samples made of spherical grains (Luong & 429
Sprik, 2013) (best fit is obtained with $S_{irr} = 0$). Note that the thin EDL is not 430
really met in this case because of $R_{min} \approx 60 \text{ nm}$ and $\lambda = 9.6 \text{ nm}$. Therefore, 431 the
model may not work really well to reproduce the experimental data as

432 shown in Fig. 8.

433 Eq. (46) is applied to determine the electroosmotic pressure
434 K_E coefficient for ten sandstone samples (20 mm in length and 25 mm in
diameter) sat435 urated by a 0.05 M NaCl electrolyte reported in Wang et al.
(2015). Parame436 ters of the sandstone samples and the measured zeta
potential are presented

Figure 8: Maximum pressure difference as a function of applied voltage. The symbols are experimental data from Luong & Sprik (2013) with $\pm 15 \%$ of uncertainty and the solid line is obtained from Eq. (51)

Figure 9: The variation of the K_E predicted in this work and the experimental data taken from Wang et al. (2015)

by Wang et al. (2015) and re-shown in Table 2. The measured values of K_E are obtained by the same research group Wang et al. (2016) for the same conditions and re-presented in Table 2 (see K_E^{exp}). To estimate the mean grain diameter of porous media from the permeability, we use the relation given by (e.g., Bernabe & Revil, 1995; Revil et al., 1999; Glover et al., 2006)

$$d = \sqrt{\frac{4am^2k}{\phi^{3m}}} \quad (52)$$

where the cementation exponent m is taken as 1.9 for consolidated sandstone (Friedman, 2005) and a is a constant between 2-12 that depends on the pore space (Glover et al., 2006; Glover & Walker, 2009). In this part, a is taken as 4 for a set of samples of Wang et al. (2015). With estimated values of d , measured ϕ and $\alpha = 0.001$ (that value is also relevant to that used in Liang et al. (2014) for a Fontainebleau sandstone), the K_E is predicted for reported in Table 2 (K_E^{theo}). Fig. 9 shows the predicted K_E calculated in this work and measured values taken from Wang et al. (2015). It is seen that Eq. (46) predicts the published experimental data well. Note that for this set of experimental data, we obtain the minimum value of $R_{min} \approx 2.10^3$ nm and $\lambda = 1.36$ nm. Therefore, the thin EDL assumption is satisfied and Eq. (46) is valid.

4.3. Prediction of the product of the permeability and formation factor

Comparing Eq. (7) and Eq. (46), the product of the permeability and formation factor of porous media is given by

$$kF = \frac{R_{max}^2(2 - D_f)}{8\tau(1 - \phi)(4 - D_f)} \frac{\left\{ 1 - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\}}{1 - S_{irr}} \quad (53)$$

Eq. (53) indicates that based on the fractal model for electroosmotic flow in porous media, one can get the product of the permeability and formation factor from the parameters D_f , R_{max} , τ , α and S_{irr} of porous media. Eq. (53) is now used to estimate the product of kF and compare with experimental data reported in Glover et al. (2006), Glover & D'ery (2010) and Bol'ev et al. (2007) for 27 samples of bead packs. Parameters for the samples (grain diameter, porosity, permeability) are taken from Glover et al. (2006), Glover & D'ery (2010) and Bol'ev et al. (2007) and re-shown in Table 3. The values

Table 3: Input parameters for bead packs taken from Glover et al. (2006), Glover & D'ery (2010) and Bol'ev et al. (2007). Symbols of d (μm), ϕ (no units), k (m^2), F (no units) and α (no units) stand for grain diameter, porosity, permeability, formation factor and ratio of minimum and maximum radius, respectively.

No.	d (μm)	ϕ (-)	k (10^{-12} m^2)	F (-)	α (-)	reference
1	20	0.40	0.2411	3.90	0.01	Glover et al. (2006)
2	45	0.39	1.599	4.01	0.01	Glover et al. (2006)
3	106	0.39	8.118	4.04	0.01	Glover et al. (2006)
4	250	0.40	50.46	3.97	0.01	Glover et al. (2006)
5	500	0.38	186.79	4.08	0.01	Glover et al. (2006)
6	1000	0.40	709.85	3.91	0.01	Glover et al. (2006)
7	2000	0.39	2277.26	4.13	0.01	Glover et al. (2006)
8	3350	0.40	7706.97	3.93	0.01	Glover et al. (2006)
9	1.05	0.411	0.00057	3.80	0.01	Glover & D'ery (2010)
10	2.11	0.398	0.00345	3.98	0.01	Glover & D'ery (2010)
11	5.01	0.380	0.0181	4.27	0.01	Glover & D'ery (2010)
12	11.2	0.401	0.0361	3.94	0.01	Glover & D'ery (2010)
13	21.5	0.383	0.228	4.22	0.01	Glover & D'ery (2010)
14	31	0.392	0.895	4.07	0.01	Glover & D'ery (2010)
15	47.5	0.403	1.258	3.91	0.01	Glover & D'ery (2010)
16	104	0.394	6.028	4.04	0.01	Glover & D'ery (2010)
17	181	0.396	21.53	4.01	0.01	Glover & D'ery (2010)
18	252	0.414	40.19	3.75	0.01	Glover & D'ery (2010)
19	494	0.379	224	4.29	0.01	Glover & D'ery (2010)
20	990	0.385	866.7	4.19	0.01	Glover & D'ery (2010)

21	56	0.4	2.0	3.3	0.01	Bol`eve et al. (2007)
22	72	0.4	3.1	3.2	0.01	Bol`eve et al. (2007)
23	93	0.4	4.4	3.4	0.01	Bol`eve et al. (2007)
24	181	0.4	27	3.3	0.01	Bol`eve et al. (2007)
25	256	0.4	56	3.4	0.01	Bol`eve et al. (2007)
26	512	0.4	120	3.4	0.01	Bol`eve et al. (2007)
27	3000	0.4	14000	3.6	0.01	Bol`eve et al. (2007)

Figure 10: A comparison between kF predicted from Eq. (53) and from measured data in Glover et al. (2006), Glover & D`ery (2010) and Bol`eve et al. (2007) (the solid line is a 1:1 line).

of α and S_{irr} are taken as 0.01 and 0, respectively. Value of τ is obtained by the relation $\tau = \varphi F$. From those parameters in combination with Eq. (53), the product of the permeability and formation factor is predicted in the same procedure as previously mentioned. Fig. 10 shows the comparison between the product of kF predicted in this work and the experimental data. The solid line represents a 1:1 line. It is seen that the predicted values are in very good match with the experimental data. It suggests that one can predict k of porous materials from Eq. (53) with the knowledge of F and vice versa.

4.4. Electrokinetic coupling under partially saturated condition

Based on Eq. (3) and Eq. (5), the relationship between the electroosmosis coefficient and the streaming potential coefficient is obtained as

$$K_S(S_w) = \frac{K_E(S_w)k(S_w)}{\sigma(S_w)\eta} \quad (54)$$

Therefore, the relative streaming potential coefficient is given as

$$K_S^r = \frac{K_S(S_w)}{K_S^{sat}(S_w = 1)} = \frac{K_E(S_w)}{K_E^{sat}(S_w = 1)} \frac{k(S_w)}{k(S_w = 1)} \frac{\sigma(S_w = 1)}{\sigma(S_w)}, \quad (55)$$

where $K_E^r = \frac{K_E(S_w)}{K_E^{sat}(S_w=1)}$ is given in Eq. (47), $\frac{k(S_w)}{k(S_w=1)}$ and $\frac{\sigma(S_w)}{\sigma(S_w=1)}$ are called the relative permeability and the relative conductivity of porous media and denoted by k^r and σ^r , respectively. In this work, we do not have expressions for k^r and σ^r based on the fractal theory yet. Therefore, we use expressions given by (e.g., Revil et al., 2007; Linde et al., 2006) for k^r and σ^r :

$$k^r = S_e^{(2+3\lambda)/\lambda} \quad (56)$$

and

$$\sigma^r = S_w^n, \quad (57)$$

where λ is the curve-shape parameter and n is the saturation exponent. Eq. (57) is valid for the negligible surface conductivity.

Combining Eq. (47), Eq. (55), Eq. (56) and Eq. (57), the relative

streaming potential coefficient is given by

$$K_S^r = S_e \frac{\left\{ 1 - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\}}{\left\{ [\alpha^{2-D_f} + S_w(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} - [\alpha^{2-D_f} + S_{irr}(1 - \alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}} \right\}} \times S_e^{(2+3\lambda)/\lambda} \frac{1}{S_w^n}. \quad (58)$$

Additionally, Revil et al. (2007) used the volume averaging approach to get the relative streaming potential coefficient as

$$K_S^r = S_e^{(2+3\lambda)/\lambda} \frac{1}{S_w^{n+1}}. \quad (59)$$

Figure 11 shows the change of the relative streaming potential coefficient K_S^r with the water saturation predicted from Eq. (58) and Eq. (59). Input parameters for modeling in Fig. 11 are $n=2.7$, $\lambda=0.87$, $S_{irr}=0.36$ which are

reported by Revil et al. (2007), $D_f=1.5$ and $\alpha=0.01$ which are used due to the best fit. Additionally, a comparison between those models and experimental data reported in Revil et al. (2007) for the dolomite sample E3 (square symbols) is also shown in Fig. 11. A good agreement is observed between the proposed model, the model presented by Revil et al. (2007) and experimental data. Clearly, both theoretical models are able to describe the decrease of the relative streaming potential coefficient with decreasing water saturation, from full saturation to nearly irreducible water saturation as indicated by experimental data. When S_w decreases then the number of

Figure 11: Variation of the coefficient K_S^r with the water saturation ($n=2.7$, $\lambda=0.87$, $S_{irr}=0.36$, $D_f=1.5$ and $\alpha=0.01$). The solid and dashed lines correspond to the proposed model (see Eq. (58)) and the model of Revil et al. (2007), respectively.

capillaries occupied by water in the REV decreases. Hence, the streaming current through the REV generated by a fluid flow becomes smaller at a given fluid pressure difference. Consequently, the K_S^r decreases with decreasing S_w as predicted.

4.5. Effective excess charge density

From Eq. (3), Eq. (4), Eq. (5) and Eq. (46), the effective excess charge density $\hat{Q}_v$ (C/m³) under fully saturated conditions is deduced as

$$\hat{Q}_v = \frac{8\epsilon_r\epsilon_0\zeta\tau(1-\phi)(4-D_f)}{R_{max}^2(2-D_f)} \frac{1-S_{irr}}{\left\{1 - [\alpha^{2-D_f} + S_{irr}(1-\alpha^{2-D_f})]^{\frac{4-D_f}{2-D_f}}\right\}}. \quad (60)$$

When one neglects the irreducible water saturation, Eq. (60) reduces to

$$\hat{Q}_v = \frac{8\epsilon_r\epsilon_0\zeta\tau(1-\phi)(4-D_f)}{R_{max}^2(2-D_f)} \quad (61)$$

509

510 Based on Eq. (61), we can calculate $\hat{Q}_v$ for the glass beads reported 511 in
Glover & D'ery (2010) and Bol'ève et al. (2007) using the same approach 512
mentioned above. The values of the zeta potential are reported to be $\zeta =$ 513 -
24.72 mV and -73.34 mV in Glover & D'ery (2010) and $\zeta = -17.5$ mV, -44.7

Figure 12: Variation of the effective excess charge density Q_{bv} with the permeability k . Symbols represent experimental data from Glover & D'ery (2010) and Bol'ève et al. (2007) (Table 3). The solid line is the fit line with $\log_{10}(\hat{Q}_v) = -14.2 - 0.85\log_{10}(k)$.

514 mV, -54.6 mV, -59.7 mV, -87.9 mV and -99.3 mV in Bol'ève et al. (2007)
515 (see their Fig. 8). From calculated $\hat{Q}_v$, we can plot the $\hat{Q}_v - k$ graph (in 516
which k is taken from Table 3) as shown in Fig. 12 from which we obtain

517 the fit line: $\log_{10}(Q_{bv}) = A_1 + A_2\log_{10}(k)$ with $A_1 = -14.2$ and $A_2 = -0.85$. 518 The
obtained $Q_{bv} - k$ relationship is in good agreement with that reported
519 by Jardani et al. (2007) by fitting to a large set of experimental data that
520 includes various lithologies and ionic concentrations: $\log_{10}(\hat{Q}_v) = -9.23 - 0.82$
521 $\log_{10}(k)$. The constant $A_2 = -0.85$ obtained in this work is related to rock 522
properties (R_{max} , α , τ , ϕ and D_f) and is very close to -0.82 reported by 523
Jardani et al. (2007). The obtained constant $A_1 = -14.2$ deviates largely 524
from value of -9.23 proposed by Jardani et al. (2007). The reason is that 525
 A_1 is mainly dependent of chemical and interface parameters (Guarracino 526

& Jougnot, 2018). Therefore, it varies with mineral composition of rocks, electrolyte concentration, types of electrolyte etc.

5. Conclusions

We derive a physically based model for electroosmotic flow in porous media in which the minimum pore radius is 100 times the Debye length, that is around 1 μm under environmental conditions. The porous medium is conceptualized as a bundle of tortuous capillary tubes with a pore-size distribution following a fractal law. The obtained model is linked to the applied voltage, back pressure, water saturation, irreducible water saturation and microstructural parameters of porous materials (D_f , ϕ , α , r_{max} , τ). From the model, the expressions for the electroosmosis pressure coefficient, the relative electroosmosis pressure coefficient, the maximum back pressure, the maximum flow rate, the flow rate-applied back pressure relation and the product of the permeability and formation factor of porous media are also obtained. To validate the model, the sensitivity of the relative electroosmosis pressure coefficient K_E^r to S_{irr} , α and D_f is analyzed and explained. The model predictions are then compared with published data in both cases of full saturation and partial saturation. The comparisons show that our model is able to explain well experimental data. From K_E^r , the expression for the relative streaming potential coefficient K_S^r is also deduced. From that, the variation of K_S^r with the water saturation is predicted and compared with another model as well as experimental data from the dolomite rock sample. Additionally, we also obtain an expression for the effective excess charge density $\hat{Q}_v$. We find a good agreement between those obtained expressions and published data. We believe that the model proposed in this study can open up to new studies and modelling regarding electroosmotic phenomena and paving the way to the development of new applications and technical development in various disciplines from contaminated porous media remediation to masonry structures dewatering.

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