Theory of ionic-surface electrical conduction in porous media

A. Revil*

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We present a model describing ionic electrical conduction in porous media, with particular emphasis given to surface conduction. The porous medium is assumed to consist of an insulating matrix and an interconnected pore volume that is saturated with an electrolyte. When in contact with an electrolyte, mineral surfaces get an excess of charge that is balanced by mobile ions in an electrical diffuse layer above the surface. Electrical conduction in this diffuse layer can contribute substantially to the effective electrical conductivity of the porous medium. Our surface conduction model is based on a description of surface chemical reactions and electrical diffuse layer processes. For this purpose, we consider an amphoteric mineral surface described by a five-site-type model. We derive the fractional occupancies of positive, negative, and neutral sites on the surface, and the fractional ionic diffuse layer densities, as a function of the salinity and the pH. Finally, the specific surface conductance used to describe the surface electrical conduction is related to the previously mentioned properties, via the electrical surface potential, and is found to be dependent on the electrolyte concentration and pH.
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I. INTRODUCTION

The electrical conductivity of porous media plays an important role in many scientific fields including chemistry,[1] physics, and geophysics.[2,3] The effects of surface conductivity, microstructure and diffusion processes on porous media were studied thoroughly by Johnson, Plona, and Kojima[3] (called the JPK model hereinafter) and related works.[3,4] In the JPK model, the porous medium is composed of an interconnected pore volume saturated by a binary electrolyte, and an insulating rigid phase called the matrix. The matrix is composed by one mineral species and the nonconnected porosity. The surface of the matrix is typically charged and the counterions required by macroscopic electrical neutrality, form a thin diffuse layer over it. Surface conduction within this electrical diffuse layer (noted as EDL hereinafter) can contribute substantially to the effective electrical conductivity of the porous medium. The problem of electrical conduction in a porous medium is much more complicated than a simple electrostatic problem, and must take into account (a) the behavior of several kinds of ionic carriers (cations and anions), (b) that each of these have conduction as well as convection currents,[4] and (c) that the diffuse layer region and the mineral surface properties are sensitive to fluid chemistry, and temperature. In the JPK model, surface conduction is accounted for by the specific surface conductance parameter, Σ_S, but the dependence of this parameter upon the salinity of the pore fluid is not addressed.

The effective conductivity of a porous medium saturated with a multi-ionic electrolyte is studied in Sec. II, and is found to be a function of the four microstructural parameters defined by JPK, and specific ionic-surface conductances which describe surface electrical conduction. The link between these specific surface conductances and the mineral surface electrical potential (called the Stern potential) is

given in Sec. III, in the general context of the EDL theory. The origin of this phenomenon is found in a mineral surface charge, which is investigated in Sec. IV. In this section, we consider the specific example of a quartz mineral surface using a five-site-type model. Section V contains a discussion of the results of our model.

II. ELECTRICAL CONDUCTIVITY IN POROUS MEDIA

In all that follows, microscopic equations are averaged to obtain the effective macroscopic equations of interest. We assume that the averaging volume, V, is larger than the pore microstructural heterogeneities, and is isotropic. We define $\mathbf{V}_p$ as the interconnected pore space, $\mathbf{V}_m$ the matrix space, and $\mathbf{S}$ the interface between the matrix and the interconnected pore space. We also define $\mathbf{n}$ as the normal to $\mathbf{S}$ directed from the matrix to the fluid, and S as the interface area of $\mathbf{S}$. In order to relate local and macroscopic fields, we take an averaging volume such as that described in Ref. 4: i.e., a disk of length L and cross-sectional area A (with $V=LA$), and z is the axis in the direction normal to the end faces. We assume also that there is no macroscopic gradient in the ionic concentrations.

A. Effective conductivity

The matrix is assumed to be electrically insulating, and electrical current is therefore restricted to the interconnected pore space saturated by the electrolyte, $\mathbf{V}_p$. Throughout this paper we take the condition called the ''point of zero charge'' as the thermodynamical condition at which the macroscopic effects of mineral charged surface groups cancel each other out. The point of zero charge (noted as PZC hereinafter) will be important in all that follows because it is used both for reference and standard state. As we will see explic-

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itly in Secs. III and IV, the mineral surface electrical potential is considered to be zero at the PZC, which implies no EDL and no surface electrical conduction. Note that another way to handle properties associated with the presence of the EDL is to bring the mineral surface potential (or the so-called Stern potential) to zero through specific adsorption of surface-active counterions. We consider that the averaging volume is submitted to an external electric field, $\mathbf{E} = -(\Delta\Psi/L)\hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is the unit vector parallel to $\mathbf{E}$ in the z direction. In this ''imposed field approximation,'' $\mathbf{E}$ is essentially determined by charges outside of the averaging volume (in particular, the separation of charge between the mineral surface and the EDL does not influence the macroscopic electrical field).[4] Typically, these charges reside on external boundaries and, in terms of the potential, $\mathbf{E}$ is governed by Laplace's equation. At the PZC, the electrical conduction boundary-value problem is expressed on the averaging disk as[3]

$$\mathbf{j}_e = -\sigma(r)\boldsymbol{\nabla}\psi_b, \tag{1}$$

$$\boldsymbol{\nabla}\cdot\mathbf{j}_e = \mathbf{0}, \tag{2}$$

$$\mathbf{j}_e \cdot \mathbf{n} = \mathbf{0} \quad \text{on } \mathbf{S}, \tag{3}$$

$$\Psi(z) = \begin{cases} \Psi_1 & \text{on } z=0 \\ \Psi_1 + \Delta\Psi & \text{on } z=L, \end{cases} \tag{4}$$

with the local electrical conductivity given by $\sigma(r)=0$ in $\mathbf{V}_m$, and $\sigma(r)=\sigma_f$ in $\mathbf{V}_p$ (σ_f is the electrical Ohmic conductivity of the electrolyte solution). In these equations, ψ_b is the local electrical potential distribution in $\mathbf{V}_p$, and $\mathbf{j}_e$ is the local electrical current density. Equation (1) is the local Ohm's law, Eq. (2) is a conservation equation for electrical current, Eq. (3) is an internal boundary condition on $\mathbf{S}$, and Eq. (4) is an external boundary condition. The solution of this problem in terms of the effective conductivity of the porous medium, σ_c, is given by[3]

$$\mathbf{J}_e = -\sigma_c\frac{\Delta\Psi}{L}\hat{\mathbf{z}}, \tag{5}$$

$$\sigma_c = \frac{1}{F}\sigma_f, \tag{6}$$

where $\mathbf{J}_e$ is the macroscopic electrical current density, and F is the pore-space electrical formation factor which is a dimensionless parameter characterizing the interconnected pore space topology. It is defined in terms of the local potential distribution by the well-known energy representation formula (e.g., Ref. 3), $1/F \equiv \langle \mathbf{e}_b \cdot \mathbf{e}_b \rangle$, where $\mathbf{e}_b \equiv -(L/|\Delta\Psi|)\boldsymbol{\nabla}\psi_b$, and where the angular brackets denote a volume average operator defined in $\mathbf{V}_p$ by

$$\langle\ \rangle \equiv \frac{1}{V}\int_{V_p}(\ )dV_p, \tag{7}$$

where V_p is the interconnected pore space volume. The field $\mathbf{e}_b$ is the normalized electrical field in $\mathbf{V}_p$ due to the external electrical field $\mathbf{E}$ ($|\langle\mathbf{e}_b\rangle|=1$). The inverse of the formation factor appears to be a measure of the effective interconnected porosity. The formation factor is scale invariant material
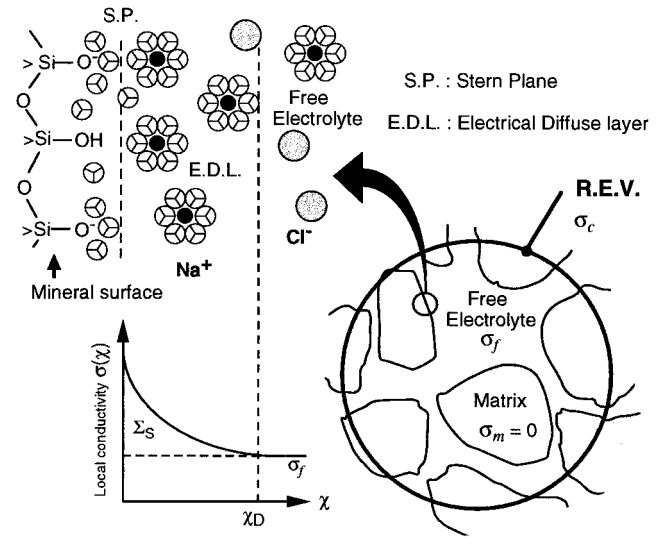

FIG. 1. Schematic representation of the electrical double layer situated at the mineral surface. The parameter σ_c is the effective electrical conductivity of a representative elementary volume (R.E.V.), whereas σ_f and σ_m are, respectively, the free electrolyte and matrix conductivities. The counterions of the electrical diffuse layer are maintained at some distance from the mineral surface by the water adsorbed on the surface forming the ''Stern layer,'' and a hydration shell around each cation. The Stern layer and the diffuse layer comprise the so-called ''double layer.''

properties. The norm of the local electric field $|\mathbf{e}_b|^2$ acts as a weighting function, giving less weight to poorly conducting pores than to highly conducting pores. For example, $|\mathbf{e}_b|^2$ vanishes in dead-ends, as a consequence of the continuity equation, thus deads-ends are not taken into account by F. Consequently, the effective conductivity is not an average of the local conductivity: $\sigma_c \neq \langle\sigma(\mathbf{r})\rangle$.

When thermodynamical conditions are different from the PZC condition, the mineral surface $\mathbf{S}$ gets an excess of charge through ionization reactions. This excess of charge is balanced by mobile ions in an EDL (Fig. 1). Electrical conduction in this EDL can contribute substantially to the effective electrical conductivity of the porous medium. The total rate of energy dissipated by Joule effect in the porous medium by ionic species i can be written as

$$\dot{W}_i = \sigma_{c,i}V|\boldsymbol{\nabla}\Psi|^2, \tag{8}$$

where $\sigma_{c,i}$ is the contribution to the effective conductivity of the porous medium due to ionic species i. We introduce the fraction of electrical current due to ionic species i, respectively, in the free electrolyte and in the diffuse layer, as $t_i^{f,hf}$ and $t_i^{S,hf}$. These parameters are called the Hittorf transport numbers for the free electrolyte and the diffuse layer, and are rigorously defined in the next subsection. By equating $\dot{W}_i$ to the sum of the local dissipations due to electrical conduction in the free electrolyte and in the thin EDL by species i, we obtain

$$\sigma_{c,i} = \frac{L^2}{V|\Delta\psi|^2}\left(\int|\boldsymbol{\nabla}\psi|^2 t_i^{f,hf}\sigma_f dV_p + \int|\boldsymbol{\nabla}\psi|^2 t_i^{S,hf}\Sigma_S dS\right), \tag{9}$$

where Σ_S is the specific surface conductance (in S), and ψ is the local potential distribution in $\mathbf{V}_p$ due to the external electric field $\mathbf{E}$ ($\psi \to \psi_b$ in absence of surface conduction, and $\mathbf{E} = -\langle \boldsymbol{\nabla}\psi \rangle$). A complete description of the total electrical potential distribution in $\mathbf{V}_p$ (i.e., EDL potential distribution plus ψ distribution) is given at the end of Sec. III. It should be noted that Eq. (9) is independent of any relationship between the specific surface conductance and the electrolyte concentration. The macroscopic free current density associated with the ionic species i can be written by $\mathbf{J}_i = \sigma_{c,i}\mathbf{E}$. However, Eq. (9) cannot be used directly because the local potential distribution ψ is not known.

Ionic high and low salinity limits (noted I.H.S. and I.L.S. limits) are defined, respectively, for each ionic conductivity contribution by

$$\text{I.H.S.:} \quad t_i^{f,hf}\sigma_f > \frac{2}{\Lambda}t_i^{S,hf}\Sigma_S, \qquad (10)$$

$$\text{I.L.S.:} \quad t_i^{f,hf}\sigma_f, < \frac{2}{\lambda}t_i^{S,hf}\Sigma_S. \qquad (11)$$

The microstructural parameters Λ and λ are defined in Appendix A. They are characteristic pore-size dimensions associated with pore and surface transport, respectively.[3] We show in Appendix A that for an arbitrary porous medium, the inequality $\lambda \geqslant \Lambda$ is always satisfied. The length scale Λ can be interpreted as an effective pore radius for transport in $\mathbf{V}_p$ (Λ is not rigorously a geometrical parameter, however, it approximates the narrow throats that control the transport). For the effective conductivity, high and low salinity limits are defined by

$$\text{H.S.:} \quad \sigma_f > \frac{2}{\Lambda}\Sigma_S, \qquad (12)$$

$$\text{L.S.:} \quad \sigma_f < \frac{2}{\lambda}\Sigma_S. \qquad (13)$$

It should be noted that the transition domain between the high and low salinity domains is different for each ionic species contribution. Consequently H.S. and L.S. domains for the rock conductivity are not similar to high and low salinity domains for the different ionic contributions. Another point is that the flux of electrical current concentrates in regions of highest conductivity. Thus, at low salinity, the flux of electrical current concentrates more in the EDL near the mineral surface, and, as the salinity increases, it spreads increasingly into the pore space. Because the distribution of local conductivity changes with the concentration (as a result of the different dependence of the specific surface conductance and the electrolyte conductivity on the ionic concentrations), the local potential distribution ψ is also salinity dependent. The electrical potential distribution ψ_S is the local electrical potential distribution in $\mathbf{V}_p$ (due to $\Delta\Psi$) when the surface conduction is dominant. The difference between the ψ_S and ψ_b distributions arises from two effects. First, the roughness of the pore surface imposes that the current lines for bulk and surface conductions are not parallel, hence causing different behaviors between high and low salinity limits. However, even if the current flux lines are locally parallel

everywhere, because of pore-scale heterogeneity, the distribution of current in the porous medium is different for bulk and surface conduction leading to the same effect.[5] Throughout this paper we consider that surface conduction takes place in the EDL, and because the diffuse layer thickness grows as the inverse square root of the electrolyte salinity, it appears to be a problem to define the conditions in which the ψ_S distribution occurs. This is because the following analysis of Secs. III and IV is valid only for thin EDL. Consequently, we have

$$\psi(\mathbf{r}) \underset{\text{H.S.}}{\longrightarrow} \psi_b(\mathbf{r}), \qquad (14)$$

$$\psi(\mathbf{r}) \xrightarrow[\begin{subarray}{c}\text{L.S.}\\ \chi_D \ll \Lambda\end{subarray}]{} \psi_S(\mathbf{r}), \qquad (15)$$

where χ_D is the total thickness of the EDL (actually in the present problem, the size of the perturbed conductivity layer in the vicinity of the mineral surface). This length will be related to the ionic strength of the free electrolyte in Sec. III. We point out that the two conditions: (a) L.S. domain [Eq. (13)], (b) $\chi_D \ll \Lambda$, allow us to determine a salinity domain where $\psi \to \psi_S$. As we said before, Eq. (9) is useless because ψ is salinity dependent, and this dependence is not known. However, it is possible to derive linear equations for each of the I.H.S. and I.L.S. limits, which are physically justified equations deduced by a perturbation method (e.g., Schwartz et al.),[3]

$$\sigma_{c,i} = \frac{1}{F}\left(t_i^{f,hf}\sigma_f + \frac{2}{\Lambda}t_i^{S,hf}\Sigma_S\right), \quad \text{I.H.S.,} \qquad (16)$$

$$\sigma_{c,i} = \frac{1}{f}\left(t_i^{S,hf}\Sigma_S + \frac{\lambda}{2}t_i^{f,hf}\sigma_f\right), \quad \text{I.L.S.} \qquad (17)$$

where the parameter f is the fourth microstructural parameter introduced by JPK to characterize transport properties in porous media (Appendix A). One of the differences between the present model for electrical conductivity and the JPK model is that we will incorporate an electro-osmotic contribution (and thus an electrical convection current) in the specific surface conductance. Despite this fact, we show in Sec. III that the problem is similar to the electrical problem considered by JPK if the classic ionic mobilities β_i, in the formulation for Σ_S, are replaced by effective mobilities B_i defined by $B_i \equiv \beta_i + 2\varepsilon_f k_B T/\eta_f eZ_i$, where ε_f is the fluid dielectric permittivity (in F m^{-1}), η_f is the fluid dynamic viscosity ($\eta_f \approx 10^{-3}$ Pa s for water at 25 °C, T is the temperature, k_B is the Boltzmann's constant (1.381×10^{-23} J K^{-1}), e is the electron charge, and Z_i the valence of ion i (all quantities including e and the ionic valences are taken to be positive). Consequently, the perturbation method applied by JPK can be used here, which is equivalent to the global averaging procedure followed in Ref. 4.

Considering the complete range of salinities between L.S. and H.S. domains, the rock ionic conductivity contribution, for cations or anions, is some function, G, of the ionic contributions in the free electrolyte, $t_i^{f,hf}\sigma_f$, and in the diffuse layer, $t_i^{S,hf}\Sigma_S$. Following JPK, I.H.S. and I.L.S. salinity limits can be connected with a smooth function, e.g., a Padé

approximant. For the ith ionic contribution to the rock conductivity, such an analysis leads to

$$\sigma_{c,i} = G[t_i^{S,hf}\Sigma_S ; t_i^{f,hf}\sigma_f] = t_i^{f,hf}\sigma_f \widetilde{G}\left[\frac{t_i^{S,hf}\Sigma_S}{t_i^{f,hf}\sigma_f}\right], \quad (18)$$

where

$$\widetilde{G}[X] = \frac{b + cX + dX^2}{1 + aX},$$

$$a = \frac{2/(\Lambda F) - 1/f}{\lambda/2f - 1/F}, \quad c = \frac{1 - \lambda/\Lambda}{f - \lambda F/2}, \quad (19)$$

$$b = 1/F, \quad d = a/f.$$

The function $\widetilde{G}$, a ratio of two polynomials, has been chosen because it connects simply and smoothly high and low salinity domains where analytical forms are given by Eqs. (16) and (17). In numerical simulations, the Padé functional gives a good approximation for the intermediate conductivities.[3,5] The total rock conductivity, σ_c, is assumed to be the sum of all rock ionic conductivity contributions (and consequently we neglect interactions between ionic species during their migrations),

$$\sigma_c = \sum_i \sigma_{c,i}, \quad (20)$$

where the sum is over all the ionic species present in the pore fluid. The total free current density is given by $\mathbf{J}_e = \sigma_c \mathbf{E}$. It should be emphasized that (1) σ_c is not a purely Ohmic conductivity because it includes a convective term due to an electro-osmosis phenomenon (the true Ohmic conductivity is obtain by equating the specific surface conductance with the electromigration surface conductance which is defined in the following sections), (2) all the previous equations are given under the ''thin-EDL'' of Fixman,[1] i.e., that the thickness of the diffuse layer must be much smaller than the dimensions of the pores and the local radius of curvature.[3] This last assumption is needed to derive Eqs. (16) and (17), and will be important for all that follows.

We show in Appendix A, that the following inequalities are always satisfied:

$$\frac{\lambda}{f} \geqslant \frac{2}{F} \geqslant \frac{\Lambda}{f}, \quad (21)$$

(and consequently $\lambda \geqslant \Lambda$). Equations (16), (17), and (21) imply a downward curvature in a plot of each ionic contribution to rock conductivity against electrolyte conductivity in linear-linear space, providing that the ionic-surface conductance contributions $t_i^{S,hf}\Sigma_S$ are constants (i.e., independent of the salinity). Since the effective electrical conductivity σ_c is the sum of all the individual contributions, it also has a convex-upward curvature, providing the specific surface conductance is held constant, i.e., $(\partial\sigma_c/\partial\sigma_f)_{\Sigma_S} > 0$, and $(\partial^2\sigma_c/\partial\sigma_f^2)_{\Sigma_S} < 0$. This is called the convexity theorem for an arbitrary porous media.[3] As we will see in Secs. III and IV, the specific surface conductance is concentration dependent. Consequently, the variation of the specific surface conductance with the electrolyte concentration does not guarantee a convex-upward curvature for the effective conductivity versus the electrolyte conductivity curve in real conditions.

B. Hittorf transport numbers

The free electrolyte conductivity is

$$\sigma_f = \sum_i e Z_i \beta_i^f C_i^f, \quad (22)$$

where C_i^f is the concentration of ionic species i in the free electrolyte. Transference and Hittorf numbers of species i (respectively, t_i^f and $t_i^{f,hf}$) in the free electrolyte are defined by[6]

$$t_i^f \equiv (\pm 1)\beta_i^f e C_i^f/\sigma_f, \quad (23)$$

$$t_i^{f,hf} \equiv (\pm 1)Z_i t_i^f, \quad \text{and} \quad \sum_i (t_i^{f,hf}) = 1. \quad (24)$$

The parameters $t_i^{f,hf}$ represent the ratio between the electrical current due to species i divided by the total electrical current in the free electrolyte. According to their definition, the Hittorf numbers are positive for all ions (with $0 \leqslant t_i^{f,hf} \leqslant 1$).

The specific surface conductance, Σ_S, represents the anomalous conduction in the EDL.[6] In the present approach, we do not consider electrical conduction in the Stern layer or directly through the surface sites, and consequently surface conduction only takes place in the EDL (Fig. 1). The specific surface conductance can be described from the sum of the individual specific surface conductances in the EDL by

$$\Sigma_S = \sum_i e Z_i \Sigma_i^S. \quad (25)$$

The ionic contributions Σ_i^S are dimensionally different from Σ_S. Surface transference and Hittorf numbers of species i (respectively, t_i^S and $t_i^{S,hf}$) can be now defined by analogy with t_i^f and $t_i^{f,hf}$,

$$t_i^S \equiv (\pm 1)e\Sigma_i^S/\Sigma_S, \quad (26)$$

$$t_i^{S,hf} \equiv (\pm 1)Z_i t_i^S, \quad \text{and} \quad \sum_i t_i^{S,hf} = 1, \quad (27)$$

where $t_i^{S,hf}$ represents the difference of electrical charges fraction transported by species i during electrical conduction (including an electro-osmotic contribution) between the EDL and the free electrolyte (the matrix is always chosen as the reference frame). We have $0 \leqslant t_i^{S,hf} \leqslant 1$. In the next section, we establish a relation between the surface Hittorf numbers and the Stern plane potential, φ_d, which can be considered as the mineral surface potential (or the inner potential of the EDL). The JPK model does not explicitly include the form of Σ_S or Σ_i^S. It can therefore be used with any model of the diffuse layer. Consequently, equations developed in this section and the following one can be incorporated into those already cited in Sec. II A.

C. Specific surface conductance

The total specific surface conductance, Σ_S, can be divided into an electromigration conductance Σ_S^e, and an electro-osmotic conductance Σ_S^{os},[4]

$$\Sigma_S = \Sigma_S^e + \Sigma_S^{os}. \qquad (28)$$

The electromigration surface conductance represents the excess Ohmic conductivity in the EDL. The electro-osmotic surface conductance is due to a convective electrical current in the EDL induced by the macroscopic electrical gradient $\mathbf{E}$ (the electrical force acting on the excess of charged ions in the EDL is transmitted by friction to the fluid in $\mathbf{V}_p$). The two surface conductances terms introduced previously can be described using the sum of their ionic contributions, $\Sigma_S^e \equiv e\Sigma_i(Z_i\Sigma_i^e)$, and $\Sigma_S^{os} \equiv e\Sigma_i(Z_i\Sigma_i^e)$, and consequently with Eqs. (25) and (28), $\Sigma_i^S = \Sigma_i^e + \Sigma_i^{os}$. In the next section, all these quantities will be related to the Stern potential.

III. THEORY OF THE ELECTRICAL DOUBLE LAYER

This section is concerned with mineral surface and EDL properties and their relations to the Stern potential. We assume in subsections A, B, and C that the porous medium is not submitted to an external electric field. The total electrical potential distribution (EDL potential distribution plus ψ) is analyzed in subsection D.

A. Internal surface densities

The fractional occupancy of surface sites is defined by $\Omega_i^0 \equiv n_i^0/\Sigma_j n_j^0$, where n_i^0 is the number of sites of species i on the surface, and $\Sigma_i(\Omega_i^0) = 1$. We can introduce the total surface concentration of ionic sites Γ_S^0 (in m^{-2}) by

$$\Gamma_S^0 \equiv \sum_i \Gamma_i^0 \equiv \sum_i n_i^0/S, \qquad (29)$$

where Γ_i^0 represents the surface concentration of surface species i and S is the surface area of the interface between the mineral and the free electrolyte. The relationship between Ω_i^0 and Γ_i^0 is obviously $\Omega_i^0 = \Gamma_i^0/\Gamma_S^0$. The surface charge density Q_S^0 (in C m^{-2}) can be calculated from the ionic density of the surface by

$$Q_S^0 = \sum_i (\pm 1)eZ_i^0\Gamma_i^0 = e\Gamma_S^0\left(\sum_i (\pm 1)Z_i^0\Omega_i^0\right), \quad (30)$$

where Z_i^0 equals zero for neutral surface site.

B. Diffuse layer densities

In this subsection we would like to determine a relationship between the equivalent surface charge density of the EDL, the ionic concentrations in the free electrolyte solution, and the Stern potential. Here, we are concerned with EDL phenomena in isothermal, isobaric porous media in the absence of an external electric field. The electrical field in the EDL, $\mathbf{e}_\varphi$, obeys the Poisson's equation, $\nabla \cdot (\varepsilon_S \mathbf{e}_\varphi) = \rho$, where ε_S is the dielectric permittivity, and ρ is the net free charge density in the EDL. The electrostatic field $\mathbf{e}_\varphi$ is irrotational, a condition that is automatically met by requiring that

$\mathbf{e}_\varphi = -\nabla\varphi$. The boundary conditions on $\mathbf{S}$ are given by $\varepsilon_S(0)\mathbf{n} \cdot \nabla\varphi = Q_S^0$, and $\mathbf{n} \times \nabla\varphi = \mathbf{0}$. Pride[4] shows that the mineral surface charge does not produce any electrical field in $\mathbf{V}_m$, and does not produce a macroscopic electrostatic field. Actually, the electrical field $\mathbf{e}_\varphi$ is screened by some ions of the electrolyte which form an ionic cloud around the mineral grains: the EDL. The model is now restricted, for useful simplifications of the general equations, to the case in which the EDL thickness is small compared to the radius of curvature of the surface and the size of pores (the thin and flat EDL hypothesis). Under these conditions, all parameters depend only on the local distance from the surface, χ, and the problem reduces to a one-dimensional problem. Consequently, Poisson's equation in the EDL can be written as

$$\frac{\partial}{\partial\chi}\left[\varepsilon_S(\chi)\frac{\partial}{\partial\chi}\varphi(\chi)\right] = -\rho(\chi), \qquad (31)$$

and the excess charge density $\rho(\chi)$ is given by

$$\rho(\chi) \equiv \sum_i \rho_i^S = \sum_i (\pm 1)eZ_iC_i^S(\chi), \qquad (32)$$

where $C_i^S(\chi)$ are the ionic concentrations in the EDL. We assume that dielectric saturation and viscoelectrical phenomena can be neglected in the EDL.[7] Consequently, $\varepsilon_S(\chi) \approx \varepsilon_f$ where ε_f is the dielectric constant of water ($\varepsilon_f \approx 80\epsilon_0$ where $\epsilon_0 = 8.84 \times 10^{-12}$ F m). Electrochemical potentials can be defined by $\mu_i = \mu_i^{(\circ)} + k_BT \ln \alpha_i + (\pm 1)eZ_i\psi$, where ψ is an electrical potential, α_i is the ionic activities of species i in the EDL (superscript "S"), or in the free electrolyte (superscript "f"), and where $\mu_i^{(\circ)}$ is a constant which depends upon an arbitrarily chosen "standard state" of the component. In equilibrium conditions, the electrochemical potentials for each ionic species i can be equated between the diffuse layer (at position χ) and the free electrolyte,[8-10]

$$\mu_i^{S,(\circ)} + k_BT \ln\alpha_i^S(\chi) + (\pm 1)Z_ie\varphi(\chi) = \mu_i^{f,(\circ)} + k_BT \ln\alpha_i^f. \tag{33}$$

The reference state (activity coefficients equal unity) for both pore fluid solution and surface species is chosen as infinite dilution relative to the aqueous phase and zero surface charge (i.e., in the PZC condition). The standard state (activities equal to unity) is chosen as one molal pore fluid solution at zero surface charge. The PZC condition ensures that there is no ionic interactions affecting either pore fluid solution or surface species in the reference and standard states. Consequently, $\mu_i^{S,(0)} = \mu_i^{f,(0)}$, and assuming an isothermal, isobaric, ideal (i.e., ionic activities and ionic concentrations can be equated), and reversible system in equilibrium gives

$$C_i^S(\chi) = C_i^f\exp[(\pm 1)Z_i\widetilde{\varphi}(\chi)], \qquad (34)$$

where $\widetilde{\varphi}(\chi) \equiv -e\varphi(\chi)/k_BT$ is the dimensionless reduced local potential in the EDL at the position χ. Equation (34) implies a Maxwell-Boltzmann distribution for the ionic concentrations in the EDL (see Ref. 8, p. 114). There is a statistic equilibrium between the electrical (attractive or repulsive) force $(\pm 1)eZ_i\nabla\varphi$ and the thermal agitation $k_BT\nabla C_i^S$

for each ionic species in the EDL. Incorporating Eq. (34) in Eq. (31) gives the Poisson-Boltzmann equation which can be written as

$$\frac{d^2\widetilde{\varphi}}{d\chi^2} = \sum_i \frac{(\pm)e^2 Z_i C_i^f}{\epsilon_f k_B T} \exp[-(\pm 1)Z_i\widetilde{\varphi}], \quad (35)$$

with appropriate boundaries conditions given by $\varphi(0) = \varphi_d$, and $(\partial\varphi/\partial\chi)_{\chi_D} = 0$, where φ_d is the Stern plane potential, and χ_D is the total thickness of the EDL. The electrical potential distribution in the EDL has, approximately, an exponential distribution given by

$$\varphi = \varphi_d \exp(-\chi/\chi_d), \quad (36)$$

where χ_d is the Debye screening length defined by

$$\chi_d \equiv \left(\frac{\varepsilon_f k_B T}{2e^2 I_f}\right)^{1/2}, \quad (37)$$

$$I_f \equiv \frac{1}{2}\sum_i Z_i^2 C_i^f, \quad (38)$$

I_f is the ionic strength of the electrolyte solution. Actually, Eq. (36) is the solution of Eq. (35) linearized by taking $|(\pm 1)eZ_i\varphi_d/k_B T| \ll 2$. The validity of this simple exponential distribution for φ (the Debye-Hückel approximation) and the relation between the mineral surface charge density Q_S^0 and φ_d are discussed in Appendix A of Ref. 4. The equivalent surface charge density of the diffuse layer is given by the integration of the excess charge density on the diffuse layer,

$$Q_S \equiv \int_0^{\chi_D} \rho(\chi)d\chi. \quad (39)$$

We define the equivalent surface charge density for species i by

$$Q_i^S \equiv \int_0^{\chi_D} \rho_i^S(\chi)d\chi, \quad (40)$$

where $\rho_i^S(\chi) = (\pm 1)eZ_i C_i^S(\chi)$. Using the definition of $\rho_i^S(\chi)$ and Eq. (34), the equivalent surface charge density for species i is given by

$$Q_i^S = (\pm 1)eZ_i C_i^f \int_0^{\chi_D} \exp((\pm 1)Z_i\widetilde{\varphi}(\chi))d\chi. \quad (41)$$

Pride has demonstrated [Eqs. (191) to (194), Ref. 4] that,

$$\int_0^{\chi_D} \exp((\pm 1)Z_i\widetilde{\varphi}(\chi))d\chi \approx 2\chi_d \exp\left(\frac{(\pm 1)Z_i\widetilde{\varphi}_d}{2}\right), \quad (42)$$

where $\widetilde{\varphi}_d \equiv -e\varphi_d/k_B T$ is the dimensionless reduced Stern potential. It can be shown that Eq. (42) is rigorously valid under the Debye-Hückel approximation of low potentials, but appears also as a useful approximation even for higher surface potentials.[4] Consequently, Eqs. (39), (40), (41), and (42) give

$$Q_S = \sum_i Q_i^S \approx 2\chi_d \sum_i (\pm 1)eZ_i C_i^f \exp\left[(\pm 1)Z_i\frac{\widetilde{\varphi}_d}{2}\right]. \quad (43)$$

The electroneutrality requirement between the surface charge density and the diffuse layer density is given, in absence of charge in the Stern layer, by

$$Q_S^0 + Q_S = 0. \quad (44)$$

This important equation relates surface and diffuse layer phenomena, whereas the link between diffuse layer and bulk electrolyte parameters is given by the Maxwell-Boltzmann distribution for the ionic concentrations.

C. Specific surface conductance

The electromigration surface conductance, Σ_S^e, represents the excess Ohmic conductivity in the vicinity of the pore-matrix interface and is defined by[3]

$$\Sigma_S^e \equiv \int_0^{\chi_D} (\sigma(\chi) - \sigma_f)d\chi, \quad (45)$$

where χ measures the distance along a normal directed into the pore space from the pore-matrix boundary, $\sigma(\chi)$ is the spatially varying conductivity in the concentration disturbed zone which approaches σ_f for $\chi \geq \chi_D$, where χ_D is the thickness of this disturbed layer. Such defined, Σ_S^e can be either a positive or a negative quantity. The local electrical conductivity, $\sigma(\chi)$, is given by analogy with the free electrolyte conductivity [Eq. (22)] by

$$\sigma(\chi) = \sum_i (eZ_i\beta_i^S(\chi)C_i^S(\chi)). \quad (46)$$

The difference between the ionic mobilities in the EDL and in the free electrolyte arises from the difference between the ionic strength in the EDL [$I_S(\chi) \equiv (\frac{1}{2})\Sigma_i Z_i^2 C_i^S(\chi)$] and in the free electrolyte (because the ionic mobility decreases with the ionic strength, e.g., Ref. 6). In the rest of the paper, we will consider that the ionic mobilities in the EDL are constant (and should be evaluated at the mean ionic strength of the EDL), but at least, in first order, it is always possible to consider that the ionic mobilities are equal in the EDL and in the free electrolyte for each ionic species. Consequently, from Eqs. (22), (45), and (46)

$$\Sigma_S^e = \int_0^{\chi_D} \sum_i eZ_i[\beta_i^S C_i^S(\chi) - \beta_i^f C_i^f]d\chi, \quad (47)$$

Using Eqs. (34), (42), and (47), the electromigration surface conductance is given by

$$\Sigma_S^e = 2\chi_d\left[\sum_i (eZ_i)\beta_i^S C_i^f \exp\left((\pm 1)Z_i\frac{\widetilde{\varphi}_d}{2}\right) - \sigma_f\right]. \quad (48)$$

The electromigration surface conductance can be written from the sum of its ionic contributions, Σ_i^e (Sec. II C) and consequently

$$\Sigma_i^e = \int_0^{\chi_D} [\beta_i^S(\chi)C_i^S(\chi) - \beta_i^f C_i^f]d\chi, \quad (49)$$

$$= 2\chi_d C_i^f\left[\beta_i^S \exp\left((\pm 1)Z_i\frac{\widetilde{\varphi}_d}{2}\right) - \beta_i^f\right]. \quad (50)$$

We next consider the surface electro-osmotic conductance such as described by Bikerman,[9] and generalized to a multi-ionic electrolyte by Pride.[4] In homogeneous electrolyte solutions, the concentrations of the cation and the anion are necessarily stoichiometrically equivalent. Consequently, when an electrical field is applied, cations and anions convey equal overall momentum to the solvent, and there is no solvent convection. In a porous medium, for conditions other than the PZC, the situation is different. There is a majority of cations or anions (depending of the sign of the mineral surface charge) in $\mathbf{V}_p$, specifically in the EDL. When an electrical field is applied, it results in a solvent convection, and consequently a surplus conductivity called the electro-osmotic conductivity. To study this phenomenon, it is necessary to add equations describing the fluid velocity distribution in $\mathbf{V}_p$ due to the external electrical field $\mathbf{E}$. For an incompressible fluid, the equation of continuity is $\nabla \cdot \mathbf{v} = \mathbf{0}$, where $\mathbf{v}$ is the local fluid velocity in $\mathbf{V}_p$. The equation of motion for a fluid of constant density and viscosity is a form of the Navier-Stokes equation (which is a form of the momentum-conservation law). In the limit of slow incompressible flow, the Navier-Stokes equation reduces to the linear Stokes equation, $\mathbf{0} = -\nabla p + \eta_f \nabla^2 \mathbf{v} + \mathbf{F}$, where p is the thermodynamic fluid pressure (Pa), and $\mathbf{F}$ is the total external force per unit volume. This last term can be written by, $\mathbf{F} = \rho_f \mathbf{g} - \rho \nabla \psi$, where $\mathbf{g}$ is the acceleration of gravity (m s^{-2}), and ρ is the excess charge density previously defined by Eq. (32), and ψ is an electric potential. The two terms on the left represent the change of momentum of a fluid element due to the forces on the right, pressures forces, viscous forces, gravitational forces, and electrostatic forces in the present case (the coupling between ionic flow and hydraulic flow is a consequence of a friction effect). We consider a fluid saturated porous medium submitted to a constant electrostatic field, and we neglect the gravitational force. Following Ref. 4, we note p_e and $\mathbf{v}_e$, respectively, the thermodynamical fluid pressure and fluid velocity induced by the macroscopic electrical field, $\mathbf{E}$. The vector $-\nabla \psi$ is now the same electrical-field distribution used in Sec. II. The electrical force acts only in the EDL because the excess charge density equals zero in the free electrolyte (due to the electroneutrality requirement). The analysis of electro-osmosis also requires a statement of the internal and external boundaries conditions, which are given by Pride[4] to be, $p_e = 0$, as $z = 0, L$, $\nabla p_e \cdot \mathbf{n} = \mathbf{0}$, $\mathbf{v}_e = \mathbf{0}$ on S. It follows that $p_e = 0$ in $\mathbf{V}_p$. Consequently, the Stokes equation reduces to $\eta_f \nabla^2 \mathbf{v}_e = \rho(\chi) \nabla \psi$ (and $\mathbf{v}_e$ is solenoidal), $\rho(\chi)$ the excess charge density in the EDL is given by Eq. (32), and $\nabla \psi$ is the local electrical potential gradient described in Sec. II and generated in $\mathbf{V}_p$ by the macroscopic electrical field $\mathbf{E}$. We assume that the shear plane (the surface defined in $\mathbf{V}_p$ by the condition $\mathbf{v}_e = 0$) can be merged with the Stern plane, and also that the variations of $\nabla \psi$ can be neglected in the EDL as a consequence of the thin and flat EDL assumption. The solution of the Stokes equation with the previous internal boundary conditions is given by[4]

$$\mathbf{v}_e(\chi) = -\frac{\varepsilon_f}{\eta_f} [\varphi(\chi) - \varphi_d] \nabla \psi. \qquad (51)$$

Consequently, the rate of the electrically induced convection in the porous medium depends chiefly on the Stern plane

potential, the local electrical field, and the fluid flow resistance (i.e., the viscosity of the fluid). We note that in the free electrolyte, the fluid velocity induced by the external electrical fields is, $\mathbf{v}_e \approx (\varepsilon_f / \eta_f) \varphi_d \nabla \psi$, for $\chi > \chi_D$. We define the electro-osmotic mobility by $\mathbf{v}_e(\chi) \equiv -\beta_{os}(\chi) \nabla \psi$, and consequently, $\beta_{os}(\chi) = (\varepsilon_f / \eta_f)[\varphi(\chi) - \varphi_d]$. Note that β_{os} can be positive or negative depending on the sign of the Stern plane potential φ_d. It is now natural to set the electro-osmotic surface conductance in the EDL as (it should be noted again that there is no excess charge density in the free electrolyte)

$$\Sigma_S^{os} \equiv \int_0^{\chi_D} \rho(\chi) \beta_{os}(\chi) d\chi = \sum_i (eZ_i) \Sigma_i^{os}. \qquad (52)$$

Note that the Stern potential is negative when the EDL contains an excess positive charge and positive when the EDL contains an excess negative charge. Consequently, $\text{Sign}(\beta_{os}) = \text{Sign}(\rho(\chi))$, where ''Sign'' refers to the sign of the quantity in parenthesis, and therefore, the electro-osmotic surface conductance is always a positive quantity. The electroosmotic surface conductance can be integrated by parts in order to be related to the Stern plane potential (with the appropriate boundary conditions for φ given previously in Sec. III B). After some algebraic manipulations, and using the following equation:

$$\left(\frac{\partial \varphi}{\partial \chi}\right)^2 = \frac{2k_B T}{\varepsilon_f} \sum_i C_i^f \left[\exp\left(-\frac{(\pm 1)eZ_i \varphi}{k_b T} \right) - 1 \right], \qquad (53)$$

which can be obtained by multiplying both sides of the Poisson-Boltzmann equation by $\partial \varphi / \partial \chi$ and integrating, Pride (Ref. 4) gives

$$\Sigma_S^{os} = \frac{4\varepsilon_f k_B T}{\eta_f} \chi_d \sum_i C_i^f \left[\exp\left((\pm 1)Z_i \frac{\widetilde{\varphi}_d}{2} \right) - 1 \right]. \qquad (54)$$

The ionic contributions of the electro-osmotic surface conductance are easily obtained from Eq. (52). The total ionic contribution (electromigration plus electro-osmosis) of the specific surface conductance can be now written from Sec. II C and Eqs. (50), and (54) as

$$\Sigma_i^S = 2\chi_d C_i^f \left[B_i^S \exp\left((\pm 1)Z_i \frac{\widetilde{\varphi}_d}{2} \right) - B_i^f \right], \qquad (55)$$

where the effective mobility B_i is defined by $B_i \equiv \beta_i + 2\varepsilon_f k_B T / (\eta_f e Z_i)$. An evaluation of the magnitude of the two terms in the equation of the effective mobility show that the electro-osmotic effect is appreciable, and therefore should not be neglected. Consequently, if we compare the forms of Eqs. (55) and (50), the problem electromigration plus electro-osmosis is similar to that of electromigration, but using effective ionic mobilities B_i instead of β_i. Finally, Eqs. (25), (26), (27), and (55) allow direct computation of the surface Hittorf numbers as a function of the Stern potential.

It should be noted that the concentrations of the ions are perturbed by the mineral surface charge over distances equal

to several times the Debye screening length χ_d, whereas the thickness of the "conductivity perturbed zone" is smaller. Equations (43) and (55) indicate that the final result, in terms of conductivity perturbation thickness, is equivalent to $2\chi_d$. Similarly, Eq. (43) shows that in terms of diffuse layer charge, the final result is equivalent to emptying a region of thickness $2\chi_d$ of ions possessing the same charge as surface sites. Consequently, the "equivalent thickness" of the diffuse layer, for the conductivity problem, is equal to $2\chi_d$, and is a salinity-dependent parameter. When the double layer reaches its minimum thickness, the counter ions are concentrated in the Helmoltz layer. Consequently, the Helmoltz layer thickness, χ_H, constitutes the lower limit of the diffuse layer thickness. It can be computed from the hydration diameter of the counter ions present at the surface. Assuming the dimension of hydrated ions is the same within the diffuse layer and in the free solution; $\chi_H = 2r_i^{aq}$, where r_i^{aq} is the mean hydration radius of the counter ions. For example, Nightingale[11] gives $r_{Na}^{aq} \approx 3.6$ Å. To account for this effect, Clavier, Coates, and Dumanoir[2] introduced a "double layer expansion factor" $\alpha_d \equiv 2\chi_d/\chi_H \geq 1$. α_d decreases when the concentration of the electrolyte increases. The minimum value of the double layer expansion factor is that when the diffuse layer thickness is minimum and equals χ_H. An "EDL high salinity domain" is defined for an electrolyte concentration greater than a critical concentration given by the equality between χ_D and χ_H. Consequently, for a symmetric electrolyte, this critical concentration is given by $C_f^{crit} \equiv 2\varepsilon_f k_B T/(e^2 Z^2 \chi_H^2)$. Approximately, $C_f^{crit} \approx 0.729$ mol l^{-1} for a NaCl solution at 25 °C, which corresponds to 6.3 S m^{-1}.

Another point is that in the present approach, we have considered the mineral surface as uniformly charged (true charges are discrete). Consequently, in our approach the electrical potential gradient is radial to the surface everywhere, and $\varphi \propto \exp(-\chi/\chi_d)$, rather than radial toward surface sites with $\varphi \propto (1/r)\exp(-r/\chi_d)$, where r is the distance from the surface site. This continuum assumption is valid if the surface charge density is larger than a critical value which depends on the diffuse layer thickness and its relationship to with the salinity. The surface density of the dominant charged surface type site is defined by $\Gamma_{(+/-)}^0 \equiv \text{Max}(\Gamma_{(+)}^0, \Gamma_{(-)}^0)$ (we have $\Gamma_{(+/-)}^0 \leq \Gamma_S^0$, Γ_S^0 being the total surface site density). The average distance between the charged sites is approximately $(\Gamma_{(+/-)}^0)^{-1/2}$. We consider then that the continuum assumption for the surface charge is valid if the characteristic length associated with the EDL, say χ_d, is greater than half of the average distance between charged surface sites, $\chi_d \geq (\Gamma_{(+/-)}^0)^{-1/2}/2$. Using the definition of the Debye screening length [Eq. (37)], this condition can also be expressed by

$$I_f \leq \frac{2\varepsilon_f k_B T}{e^2} \Gamma_{(+/-)}^0. \qquad (56)$$

Taking, for example, $\Gamma_{(+/-)}^0 = 0.6$ charged sites/nm^2, gives $I_f \leq 0.2$ mol/l. Obviously, $\Gamma_{(+/-)}^0$ will also depend on the concentration of potential determining ions in the free electrolyte (e.g., pH for an amphoteric surface) and ionic strength (as it will be shown in Sec. IV), thus, the continuum assump-

tion is valid for different ranges of ionic strength depending on fluid chemistry and mineral.

D. Total electrical potential distribution

If a macroscopic electrical potential gradient, $\mathbf{E} = -(\Delta\Psi/L)\hat{\mathbf{z}}$, is applied to the porous medium, the total electrical potential in $\mathbf{V}_p$, ψ_T, can be considered as the sum of ψ (the local potential generated by $\mathbf{E}$ in $\mathbf{V}_p$), and φ (the electrical potential in the EDL), that vanishes outside the EDL because of the Debye-Hückel screening. Consequently, we have, $\psi_T = \psi + \varphi$. It should be emphasized that the distribution of ψ is dependent on the strength of the electrical potential φ. This dependence is a consequence of the heterogeneity of the porous medium: the specific surface conductance and electrolyte conductivity do not have the same dependence upon the ionic strength. Thus the local conductivity distribution in the porous medium (and consequently the potential distribution ψ) changes with any variation of the ionic strength. Reference 5 gives a numerical investigation of this phenomenon where the specific surface conductance Σ_S, and, implicitly the Stern potential, is taken as a constant. For example, if the Stern plane potential φ_d (and thus φ) is high, resulting in large specific surface conductance Σ_S, then ψ will tend to the low salinity distribution ψ_S. If $\varphi_d \to 0$, which is the case in the PZC condition, we have ψ_T (and ψ) $\to \psi_b$. The boundary conditions for φ and ψ on $\mathbf{S}$ are given by, $\nabla\varphi \times \mathbf{n} = \mathbf{0}$, and $\nabla\psi \cdot \mathbf{n} = 0$, hence, we also have, on $\mathbf{S}$,

$$\nabla\psi \cdot \nabla\varphi = 0. \qquad (57)$$

In the presence of an external electrical field, the equality of electrochemical potentials between any position χ in the EDL and in the free electrolyte ($\chi > \chi_D$), along a normal to $\mathbf{S}$, reduces to the classic Maxwell-Boltzmann distribution for $C_i^S(\chi)$ [Eq. (34)] only if the variations of ψ can be neglected in the EDL. Again, the flat EDL assumption must be satisfied (ψ should vary slowly over a distance small compared to the radii of curvature of the surface). Consequently, within the EDL, $\nabla\psi$ is tangential to the surface (because $\nabla\psi \cdot \mathbf{n} = 0$), and taking Eq. (51), $\mathbf{v}_e$ is also tangential to the surface. The result is that the normal electrochemical gradient to the surface equals zero. In the EDL, the total electrochemical potential gradient can be decomposed into normal and tangential parts: $\nabla\mu_i^S = \nabla_n\mu_i^S + \nabla_t\mu_i^S$, and because $\nabla_n\mu_i^S = 0$, we have, $\nabla\mu_i^S = (\pm 1)eZ_i\nabla\psi$ (which is the net force acting on the ions in the EDL when the porous medium is subjected to an external electric field).
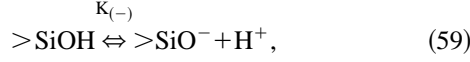
IV. APPLICATION TO A QUARTZ/ELECTROLYTE SYSTEM

The determination of the Stern potential, φ_d, is the key that enables EDL properties to be calculated. This section is devoted to the determination of the Stern potential as a function of pH and electrolyte salinity from surface physical chemistry of quartz as an example. The fractional occupancy of ions in the EDL are compared with an earlier simpler two-site model ISCOM I.
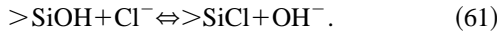
A. Surface reactions

We consider that **S** is covered by $>$SiO-H groups (where $>$refers to the mineral lattice). These groups can be considered as Brönsted acid sites. Adsorption of H^+ and OH^- ions is based on protonation and deprotonation of surface silanol groups,[12]

$$>\text{SiOH} + H^+ \overset{K_{(+)}}{\Leftrightarrow} >\text{SiOH}_2^+, \qquad (58)$$

$$>\text{SiOH} \overset{K_{(-)}}{\Leftrightarrow} >\text{SiO}^- + H^+, \qquad (59)$$

where $K_{(\pm)}$ are the intrinsic equilibrium constants of these amphoteric reactions. Other models of surface complexation involve more than one type of protonation site.[12] Although such multisite models are not explicitly addressed here, it is expected that the model and the resolution method developed below can also be applied to them. To complete the model of surface complexation, we also consider the salt ions (for example Na^+ and Cl^-) to bind onto the surface by the following chemical equations given by Schlinder and Stumm:[13]

$$>\text{SiOH} + Na^+ \overset{K_{Na}}{\Leftrightarrow} >\text{SiONa} + H^+, \qquad (60)$$

$$>\text{SiOH} + Cl^- \Leftrightarrow >\text{SiCl} + OH^-. \qquad (61)$$

For the most convenience, Eq. (61) can be combined with the water dissociation equilibrium, $H_2O \Leftrightarrow OH^- + H^+$ to give the following chemical reaction:

$$>\text{SiOH} + Cl^- + H^+ \overset{K_{Cl}}{\Leftrightarrow} >\text{SiCl} + H_2O. \qquad (62)$$
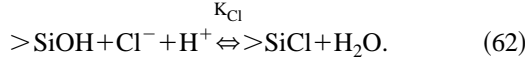
K_{Na} and K_{Cl} are the intrinsic equilibrium constants of the reactions of adsorption [Eqs. (60) and (62)]. The adsorption equations imply that Na^+ adsorption occurs for high pH values (in the basic domain), whereas the Cl^- adsorption occurs for low pH values (in the acid domain). These chemical reactions lead to five species on the surface $>$SiOH, $>$SiO$^-$, $>$SiOH$_2^+$, $>$SiONa, and $>$SiCl. We note, as previously defined, Γ_S^0, as the total surface site density and, therefore a conservation equation can be written by

$$\Gamma_S^0 = \Gamma_{\text{SiOH}}^0 + \Gamma_{\text{SiO}^-}^0 + \Gamma_{\text{SiOH}_2^+}^0 + \Gamma_{Na}^0 + \Gamma_{Cl}^0, \qquad (63)$$

where Γ_i^0 are the density of the five surface species per unit area of the quartz interface (Γ_{Na}^0 and Γ_{Cl}^0 are the relative surface site densities for the adsorption of Na^+ and Cl^-).

The equilibrium conditions for Eqs (58), (59), (60), and (62) may be written in terms of the equality of electrochemical potentials for each chemical equation;

$$\mu_{\text{SiOH}}^0 = \mu_{\text{SiO}^-}^0 + \mu_{H^+}^0, \qquad (64)$$

$$\mu_{\text{SiOH}}^0 + \mu_{H^+}^0 = \mu_{\text{SiOH}_2^+}^0, \qquad (65)$$

$$\mu_{\text{SiOH}}^0 + \mu_{Na^+}^0 = \mu_{\text{SiONa}}^0 + \mu_{H^+}^0, \qquad (66)$$

$$\mu_{\text{SiOH}}^0 + \mu_{Cl^-}^0 + \mu_{H^+}^0 = \mu_{\text{SiCl}}^0 + \mu_{H_2O}^0. \qquad (67)$$

The electrochemical potential of surface sites is defined by, $\mu_i^0(\text{site}) = (\partial G/\partial \Gamma_i^0)_{T,p,\Gamma_j^0(i \neq j)}$, where G is the Gibbs free energy. For simplification, the surface is assumed to be ideal (surface activity coefficients equal to unity). The number of possible arrangements on the surface sites is given by

$$H = \frac{\Gamma_S^0!}{\Gamma_{\text{SiOH}}^0! \Gamma_{\text{SiO}^-}^0! \Gamma_{\text{SiOH}_2^+}^0! \Gamma_{\text{SiONa}}^0! \Gamma_{\text{SiOCl}}^0!}. \qquad (68)$$

H contributes to the Gibbs free energy an entropic term given by $G = G^{(\circ)} - k_B T \ln H$, where $G^{(\circ)}$ is the Gibbs free energy in the standard state. As, $\partial \ln H/\partial \Gamma_i^0 \approx -\ln \Gamma_i^0$, where we have used Stirling's formula, $\ln N! \approx N(\ln N - 1)$, we have, $\mu_i^0(\text{site}) = \mu_i^{(\circ)} + k_B T \ln \Gamma_i^0$. The electrochemical potential of an ion near the mineral surface is $\mu_i^0(\text{ion}) = \mu_i^{(\circ)} + k_B T \ln C_i^f - (\pm 1)e Z_i \varphi_d$. The superscript $^{(\circ)}$ denotes standard chemical potentials, and C_i^f is the ionic concentration of ionic species in the free electrolyte. The $-(\pm 1)e Z_i \varphi_d$ term in the last equation represents the energy required to bring a ionic species with a charge $(\pm 1)e Z_i$ from the reference state potential to the given mineral surface potential φ_d. The intrinsic equilibrium constants can be defined by the following relationships:

$$\ln K_{(+)} \equiv \frac{1}{k_B T}(\mu_{\text{SiOH}}^{(\circ)} + \mu_{H^+}^{(\circ)} - \mu_{\text{SiOH}_2^+}^{(\circ)}), \qquad (69)$$

$$\ln K_{(-)} \equiv \frac{1}{k_B T}(\mu_{\text{SiOH}}^{(\circ)} - \mu_{\text{SiO}^-}^{(\circ)} - \mu_{H^+}^{(\circ)}), \qquad (70)$$

$$\ln K_{Na} \equiv \frac{1}{k_B T}(\mu_{\text{SiOH}}^{(\circ)} + \mu_{Na^+}^{(\circ)} - \mu_{H^+}^{(\circ)} - \mu_{\text{SiONa}}^{(\circ)}), \qquad (71)$$

$$\ln K_{Cl} \equiv \frac{1}{k_B T}(\mu_{\text{SiOH}}^{(\circ)} + \mu_{Cl^-}^{(\circ)} + \mu_{H^+}^{(\circ)} - \mu_{\text{SiOCl}}^{(\circ)} - \mu_{H_2O}^{(\circ)}). \qquad (72)$$

Consequently, the thermodynamic equilibrium constants are defined for the standard state conditions, and are only functions of temperature and pressure through the dependence of the standard chemical potential on these quantities. Using Eqs. (64)–(67) and the definitions (69) to (72), we can determine the following relationships between the surface intrinsic dissociation constants $K_{(\pm)}$, the Stern plane potential, φ_d, and the ionic-surface site density, Γ_i^0,

$$K_{(+)} = \frac{\Gamma_{\text{SiOH}_2^+}^0}{\Gamma_{\text{SiOH}}^0 C_{H^+}^f} \exp\left(\frac{e \varphi_d}{k_B T}\right), \qquad (73)$$

$$K_{(-)} = \frac{\Gamma_{\text{SiO}^-}^0 C_{H^+}^f}{\Gamma_{\text{SiOH}}^0} \exp\left(-\frac{e \varphi_d}{k_B T}\right), \qquad (74)$$

$$K_{Na} = \frac{\Gamma_{Na}^0 C_{H^+}^f}{\Gamma_{\text{SiOH}}^0 C_{Na^+}^f}, \qquad (75)$$

$$K_{Cl} = \frac{\Gamma_{Cl}^0}{\Gamma_{\text{SiOH}}^0 C_{H^+}^f C_{Cl^-}^f}. \qquad (76)$$

The PZC is defined here as the pH at which the macroscopic effects of charged surface groups cancel each other out (and consequently the Stern plane potential, φ_d, equals zero), i.e., $(\Gamma^0_{SiO^-})_{pzc} = (\Gamma^0_{SiOH_2^+})_{pzc}$, so that, $(C^f_{H^+})_{pzc} = \sqrt{K_{(-)}/K_{(+)}}$. As $pH = -\log_{10}[C^f_{H^+}]$, the pH corresponding to the PZC is

$$pH(pzc) = -\frac{1}{2}\log_{10}\left(\frac{K_{(-)}}{K_{(+)}}\right). \qquad (77)$$

This last relationship gives the aqueous concentration of H^+ needed to produce a surface with an average neutral charge over its entire area. We have $\Gamma^0_{SiOH_2^+} > \Gamma^0_{SiO^-}$ for pH $<$pH(pzc) resulting in a positive surface charge, and $\Gamma^0_{SiOH_2^+} < \Gamma^0_{SiO^-}$ for pH$>$pH(pzc) resulting in a negative surface charge. Equation (77) is equivalent to the relationship derived by Glover *et al.*[14] Using Eqs. (73) to (76), the fractional occupancies of surface site are given by

$$\Omega^0_{(+)} \equiv \frac{\Gamma^0_{SiOH_2^+}}{\Gamma^0_S} = \frac{\Gamma^0_{SiOH}C^f_{H^+}K_{(+)}}{\Gamma^0_S}\exp\left(-\frac{e\varphi_d}{k_BT}\right), \quad (78)$$

$$\Omega^0_{(-)} \equiv \frac{\Gamma^0_{SiO^-}}{\Gamma^0_S} = \frac{\Gamma^0_{SiOH}K_{(-)}}{C^f_{H^+}\Gamma^0_S}\exp\left(\frac{e\varphi_d}{k_BT}\right), \qquad (79)$$

$$\Omega^0_{Na} \equiv \frac{\Gamma^0_{Na}}{\Gamma^0_S} = \frac{C^f_{Na^+}\Gamma^0_{SiOH}K_{Na}}{C^f_{H^+}\Gamma^0_S}, \qquad (80)$$

$$\Omega^0_{Cl} \equiv \frac{\Gamma^0_{Cl}}{\Gamma^0_S} = \frac{C^f_{H^+}C^f_{Cl^-}\Gamma^0_{SiOH}K_{Cl}}{\Gamma^0_S}. \qquad (81)$$

Using the mass balance equation, Eq. (63), we find that $\Gamma^0_{SiOH} = \Gamma^0_S/A$, where,

$$A = 1 + K_{(+)}C^0_{H^+} + \frac{K_{(-)}}{C^0_{H^+}} + K_{Na}\frac{C^f_{Na^+}}{C^f_{H^+}} + K_{Cl}C^f_{H^+}C^f_{Cl^-},$$

and $C^0_{H^+}$ is the concentration of hydrogen ions on the surface **S** (i.e., for $\chi = 0$), which is given from the Maxwell-Boltzmann distribution [Eq. (34)] by $C^0_{H^+} = C^f_{H^+}\exp(\widetilde{\varphi}_d)$, $C^f_{H^+}$ is the hydrogen ion concentration in the free electrolyte. So finally from Eqs. (78) to (81), we have

$$\Omega^0_{(+)} = K_{(+)}C^0_{H^+}/A, \qquad (82)$$

$$\Omega^0_{(-)} = K_{(-)}/(C^0_{H^+}A), \qquad (83)$$

$$\Omega^0_{Na} = K_{Na}C^f_{Na^+}/(C^f_{H^+}A), \qquad (84)$$

$$\Omega^0_{Cl} = K_{Cl}C^0_{Cl^-}/(C^f_{H^+}A), \qquad (85)$$

$$\Omega^0_{SiOH} \equiv \Gamma^0_{SiOH}/\Gamma^0_S = 1/A. \qquad (86)$$

Applying Eq. (30) (with $Z^0_{(\pm)} = 1$ in the present case) gives the surface electrical charge density,

$$Q^0_S = e(\Gamma^0_{SiOH_2^+} - \Gamma^0_{SiO^-}), \qquad (87)$$

$$= e\Gamma^0_S(\Omega^0_{(+)} - \Omega^0_{(-)}), \qquad (88)$$

$$= e\Gamma^0_S\frac{1}{A}\left(K_{(+)}C^0_{H^+} - \frac{K_{(-)}}{C^0_{H^+}}\right). \qquad (89)$$

We show now that the Nernst's equation is not adapted to describe the relationship between the Stern plane potential and the pH. We define $\Delta pH \equiv pH - pH(pzc) = -\log_{10}[C^f_{H^+}/(C^f_{H^+})_{pzc}]$, where, $C^f_{H^+}$ and $(C^f_{H^+})_{pzc}$, can be estimated from Eqs. (73), (74), and (77),

$$C^0_{H^+} = \left(\frac{K_{(-)}\Omega^0_{(+)}}{K_{(+)}\Omega^0_{(-)}}\right)^{1/2}, \qquad (90)$$

$$(C^f_{H^+})_{pzc} = \left(\frac{K_{(-)}}{K_{(+)}}\right)^{1/2}. \qquad (91)$$

Consequently, we have[15]

$$\Delta pH = -\log_{10}\left[\frac{\Omega^0_{(+)}}{\Omega^0_{(-)}}\exp\left(\frac{2e\varphi_d}{k_BT}\right)\right]^{1/2}, \qquad (92)$$

$$= -\frac{1}{2.303}\left[\frac{e}{k_BT}\varphi_d + \frac{1}{2}\ln\left(\frac{\Omega^0_{(+)}}{\Omega^0_{(-)}}\right)\right], \quad (93)$$

where $\Omega^0_{(+)}/\Omega^0_{(-)}$ can be calculated from Eqs. (78) and (79). Equation (93) must be preferred to the traditional Nernst equation given by Eq. (B4) in Appendix B. A discussion about the deviations observed from the Nernst equation for SiO_2 is given at the end of Appendix B.

B. Electrolyte reactions and diffuse layer densities

To control the pH we consider the following chemical reactions in the particular case of a sodium chloride aqueous electrolyte, $NaCl \Rightarrow Na^+ + Cl^-$, $HCl \Rightarrow H^+ + Cl^-$ (for pH$<$7), $NaOH \Rightarrow Na^+ + OH^-$ (for pH$>$7). The electrolyte concentration is noted C_f. We assume a complete dissociation for NaCl, HCl, and NaOH and we assume the ideality of the solution. The water dissociation reaction is $H_2O \Leftrightarrow OH^- + H^+$, and the dissociation constant of water K_w is close to $10^{-13.8}$ at 25 °C ($K_w = C^f_{H^+}C^f_{OH^-}$ if the water activity can be assumed to be 1). We also assume that no HCl is added when the pH$>$7 and that no NaOH is added when the pH$<$7 (of course, one could always have both present and arrive at a given pH with an effect on the salt-ion concentrations, Na^+ and Cl^-). Consequently, for an acid pH, the ionic concentrations in the free electrolyte are $C^f_{Na^+} = C_f$, $C^f_{Cl^-} = C_f + C_a$, $C^f_{H^+} = 10^3 N10^{-pH} = C_a$, and $C^f_{OH^-} = 10^3 N10^{pH - pK_w}$, where N is the Avogadro's number $(6.02 \times 10^{23}$ $mol^{-1})$, $pK_w \equiv -\log_{10} K_w$, C_a (in m^{-3}) is the HCl concentration, C_f is the salt concentration. For basic pH, ionic concentrations in the free electrolyte are given by $C^f_{Na^+} = C_b + C_f$, $C^f_{Cl^-} = C_f$, $C^f_{H^+} = 10^3 N10^{-pH}$, and $C^f_{OH^-} = 10^3 N10^{pH - pK_w} = C_b$, where C_b (in m^{-3}) is the NaOH concentration. The pH in the free electrolyte is assumed to be independent of the state of the quartz surface. The electrolyte and macroscopic effective conductivities are calculated using equations given in the

first section [in particular Eqs. (18) and (20)], the summation is done over all the ionic species present in the solutions, i.e., H^+, OH^-, Na^+, and Cl^-. The fractional occupancy of ions in EDL are defined, and calculated as

$$\Omega_i^S \equiv \frac{\int_0^{\chi_D} C_i^S(\chi)d\chi}{\sum_j \int_0^{\chi_D} C_j^S(\chi)d\chi} = \frac{C_i^f e^{(\pm 1)Z_i(\widetilde{\varphi}_d/2)}}{\sum_j C_j^f e^{(\pm 1)Z_j(\widetilde{\varphi}_d/2)}}. \quad (94)$$

This second equation is obtained using Pride's approximation [Eq. (42)] and the Maxwell-Boltzmann's distribution for the EDL concentrations [Eq. (34)]. Consequently, using the electroneutrality equation in the free electrolyte,

$$C_{Cl^-}^f + C_{OH^-}^f = C_{Na^+}^f + C_{H^+}^f, \quad (95)$$

the fractional occupancy of ions in the EDL can be easily determined by

$$\Omega_{H^+}^S = C_{H^+}^f \exp(\widetilde{\varphi}_d/2)/L, \quad (96)$$

$$\Omega_{Na^+}^S = C_{Na^+}^f \exp(\widetilde{\varphi}_d/2)/L, \quad (97)$$

$$\Omega_{OH^-}^S = C_{OH^-}^f \exp(-\widetilde{\varphi}_d/2)/L, \quad (98)$$

$$\Omega_{Cl^-}^S = C_{Cl^-}^f \exp(-\widetilde{\varphi}_d/2)/L. \quad (99)$$

where $L \equiv 2(C_{Na^+}^f + C_{H^+}^f)\cosh(\widetilde{\varphi}_d/2)$.

C. Stern plane potential determination

The surface charge density is obtained using Eqs. (34) and (89) to give the following equation:

$$Q_S^0 = e\Gamma_S^0 \frac{K_{(+)}C_{H^+}^f e^{\widetilde{\varphi}_d} - \dfrac{K_{(-)}}{C_{H^+}^f} e^{-\widetilde{\varphi}_d}}{1 + K_{(+)}C_{H^+}^f e^{\widetilde{\varphi}_d} + \dfrac{K_{(-)}}{C_{H^+}^f} e^{-\widetilde{\varphi}_d} + K_{Na}\dfrac{C_{Na^+}^f}{C_{H^+}^f} + K_{Cl}C_{H^+}^f C_{Cl^-}^f}. \quad (100)$$

The diffuse layer charge density Q_S (also in C m^{-2}) is obtained from Eq. (43) as

$$Q_S = 2e\chi_d[-(C_{Cl^-}^f + C_{OH^-}^f)e^{-\widetilde{\varphi}_d/2} + (C_{Na^+}^f + C_{H^+}^f)e^{\widetilde{\varphi}_d/2}]. \quad (101)$$

Using the electroneutrality requirement of charge in the free electrolyte (i.e., $C_{Cl^-}^f + C_{OH^-}^f = C_{Na^+}^f + C_{H^+}^f$), and the Debye screening length definition [combining Eqs. (37) and (38) to give $1/\chi_d^2 = 2e^2(C_{Na^+}^f + C_{H^+}^f)/(\varepsilon_f k_B T)$], results in (for $0 < pH < 7$),

$$Q_S = \sqrt{8\varepsilon_f k_B T N 10^3 (C_f + 10^{-pH})}\sinh\left(\frac{\widetilde{\varphi}_d}{2}\right). \quad (102)$$

Here $C_f + 10^{-pH}$ must be replaced by $C_f + 10^{pH - pK_w}$ for pH greater than 7 to account for the modification of the ionic strength due to an increase in OH^- ion concentration. Consequently, to account in one equation for the variation of Q_S with pH, it is possible to write

$$Q_S = \sqrt{8\varepsilon_f k_B T N 10^3 (C_f + 10^{-pH} + 10^{pH - pK_w})}\sinh\left(\frac{\widetilde{\varphi}_d}{2}\right). \quad (103)$$

For the present electrolyte composition, Eq. (103) is similar to the Gouy-Chapman equation between the φ_d potential and the diffuse layer charge density Q_S (e.g., Ref. 16).

The Stern plane potential, φ_d, must satisfy the electroneutrality requirement between the surface charge and the diffuse layer charge in equilibrium conditions [Eq. (44)]. Consequently, as a direct consequence of Eqs. (44), (100), and (103), the Stern plane potential must satisfied the following equation (recall that $\widetilde{\varphi}_d \equiv -e\varphi_d/k_B T$)

$$F[X] = 0, \quad (104)$$

where the function $F[X]$ is given by

$$F[X] \equiv \frac{\eta}{2}\sqrt{C_f + 10^{-pH} + 10^{pH - pK_w}}\left(X - \frac{1}{X}\right)$$
$$\times\left(1 + K_{(+)}10^{-pH}X^2 + \frac{K_{(-)}}{10^{-pH}}X^{-2}\right.$$
$$\left. + \frac{K_{Na}}{10^{-pH}}C_{Na^+}^f + K_{Cl}C_{Cl^-}^f 10^{-pH}\right)$$
$$+ K_{(+)}10^{-pH}X^2 - \frac{K_{(-)}}{10^{-pH}}X^{-2}, \quad (105)$$

where $\eta \equiv \sqrt{8\varepsilon_f k_B T N 10^3}/(e\Gamma_S^0)$, and $X \equiv \exp(\widetilde{\varphi}_d/2)$. The solution of Eq. (104) (for the direct problem pH and C_f are the input parameters, and φ_d is the output parameter) gives the relationship between the NaCl concentration, the pH and the Stern plane potential. From now and in the following computations, we neglect adsorption of salt ions in order to do a comparison with the model ISCOM I (see the next subsection). Consequently, Eq. (105) reduces to

$$F[X] \equiv \frac{\eta}{2}\sqrt{C_f + 10^{-pH} + 10^{pH - pK_w}}\left(X - \frac{1}{X}\right)\left(1 + \delta 10^{-2pH}X^4\right.$$
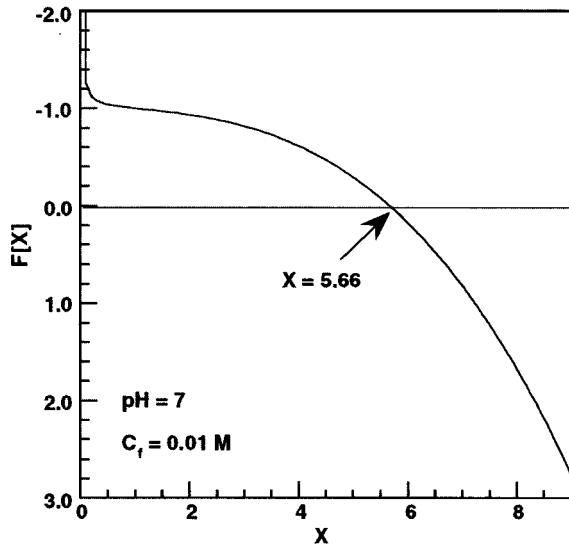$$\left. + \frac{1}{K_{(-)}}10^{-pH}X^2\right) + \delta 10^{-2pH}X^4 - 1 = 0, \quad (106)$$

FIG. 2. $F[X]$, defined by Eq. (106), versus the parameter X related to the Stern plane potential by the relationship given in the main text. In a realistic range of variation of the Stern plane potential, the equation $F[X]=0$ has only one root which can be determined by a Newton's iteration method.

and $\delta \equiv K_{(+)}/K_{(-)}$. The function $F[X]$ is plotted in Fig. 2 (pH=7, $C_f=0.1$ mol 1^{-1}, and pH(pzc)=3). In a realistic X-value range ($0.1 \leqslant X \leqslant 10$, i.e., -118 mV$\leqslant \varphi_d \leqslant 118$ mV), the equation $F[X]=0$ has only one solution. Consequently, the φ_d potential can be found using Eq. (106).

D. ISCOM I equations

ISCOM I is a model developed by Glover et al.[14] to determine the adsorbed ionic concentrations on mineral surfaces in silica dominated rocks. In ISCOM I, the density of neutral group $>$SiOH is neglected and surface sites are either negative, or positive. Consequently, the fractional availability of positive and negative surface sites $\Omega_{(+)}^{0,\mathrm{ISC}}$ and $\Omega_{(-)}^{0,\mathrm{ISC}}$, are given by[14]

$$\Omega_{(+)}^{0,\mathrm{ISC}} = \frac{(C_{\mathrm{H}^+}^0)^2}{(C_{\mathrm{H}^+}^f)_{\mathrm{pzc}}^2 + (C_{\mathrm{H}^+}^0)^2}, \qquad (107)$$

$$\Omega_{(-)}^{0,\mathrm{ISC}} = \frac{(C_{\mathrm{H}^+}^f)_{\mathrm{pzc}}^2}{(C_{\mathrm{H}^+}^f)_{\mathrm{pzc}}^2 + (C_{\mathrm{H}^+}^0)^2}. \qquad (108)$$

These equations can be compared with Eqs. (78) and (79), which can be written in absence of specific adsorption by

$$\Omega_{(+)}^0 = \frac{(C_{\mathrm{H}^+}^0)^2}{C_{\mathrm{H}^+}^0/K_{(+)} + (C_{\mathrm{H}^+}^0)^2 + (C_{\mathrm{H}^+}^f)_{\mathrm{pzc}}^2}, \qquad (109)$$

$$\Omega_{(-)}^0 = \frac{(C_{\mathrm{H}^+}^f)_{\mathrm{pzc}}^2}{C_{\mathrm{H}^+}^0/K_{(+)} + (C_{\mathrm{H}^+}^0)^2 + (C_{\mathrm{H}^+}^f)_{\mathrm{pzc}}^2}. \qquad (110)$$

In the simplified case where all ions of the free solution have the same affinity for occupying surface sites, their occupation depends only upon the availability of the ion in aqueous solution and the availability of the polarity surface

site with the correct electrical polarity. Consequently, in ISCOM I the fractional occupation of ions on surface sites can be determined by

$$\Omega_{\mathrm{H}^+}^{S,\mathrm{ISC}} = \Omega_{(-)}^{0,\mathrm{ISC}} \frac{C_{\mathrm{H}^+}^f}{C_{\mathrm{Na}^+}^f + C_{\mathrm{H}^+}^f}, \qquad (111)$$

$$\Omega_{\mathrm{Na}^+}^{S,\mathrm{ISC}} = \Omega_{(-)}^{0,\mathrm{ISC}} \frac{C_{\mathrm{Na}^+}^f}{C_{\mathrm{Na}^+}^f + C_{\mathrm{H}^+}^f}, \qquad (112)$$

$$\Omega_{\mathrm{OH}^-}^{S,\mathrm{ISC}} = \Omega_{(+)}^{0,\mathrm{ISC}} \frac{C_{\mathrm{OH}^-}^f}{C_{\mathrm{OH}^-}^f + C_{\mathrm{Cl}^-}^f}, \qquad (113)$$

$$\Omega_{\mathrm{Cl}^-}^{S,\mathrm{ISC}} = \Omega_{(+)}^{0,\mathrm{ISC}} \frac{C_{\mathrm{Cl}^-}^f}{C_{\mathrm{OH}^-}^f + C_{\mathrm{Cl}^-}^f}. \qquad (114)$$

In Appendix B, we demonstrate that ISCOM I assumes implicitly a Nernst relationship between the Stern plane potential and the pH. However, as demonstrated by Levine and Smith,[15] the Nernst equation is not adapted for the description of surface potential for oxides and silicates and must be replaced by Eq. (93).

E. Numerical computation

We assume for the following computation that $\Gamma_S^0 = 1.5$ sites/nm^2 for the effective surface site density. This value should be considered as a lower bound for this parameter.[17] Iler[18] gives a silanol surface site density of 6–8 sites/nm^2 on a silica surface using geometric considerations. However, there exists other data indicating that in certain cases a larger surface site density is possible (e.g., 25 sites/nm^2, Yates and Healy).[19] In the latter case, the density of OH groups is greater than the possible site density for a monolayer of silanol surface site situated on a flat surface, and hence, the OH groups must be present in a three-dimensional layer. This phenomenon can be explained by the presence of a gel layer of hydrolyzed material which, when in solution, may be permeable to ions, and therefore explain the exceptionally high surface charge which are observed in some cases by potentiometric titration.[19,20]

The intrinsic equilibrium constants are estimated from Ref. 15 for SiO$_2$: $p\mathrm{K}_{(-)}=6.3$ and pH(pzc)≈ 3 (Ref. 21). Such a value for the dissociation constant, $p\mathrm{K}_{(-)}$, must also be considered as a lower bound. Hiemstra, de Wit, and van Riemsdijk,[12] have calculated $\mathrm{K}_{(-)}=10^{-7.5}$ directly from the SiOH solution monomer analog taking into account only the difference in Si-H distance for silicate in the interface compared with the distance in the solution monomer and the correction term for the presence of a negative charge at the monomer. Marshall et al.[12] have determined $\mathrm{K}_{(-)}=10^{-7.2\pm0.2}$ using a spectroscopic method.

These parameters values can be used to calculate δ and η in Eq. (106), and this equation can be solved numerically by Newton's method. The starting Stern plane potential for the numerical solution is zero (i.e., $X=1$). The Stern plane potential is easily derived by using $\varphi_d = -(2k_B T/e)\ln X$. The φ_d potential is given as a function of pH for different electrolyte concentrations in Fig. 3. The surface charge density
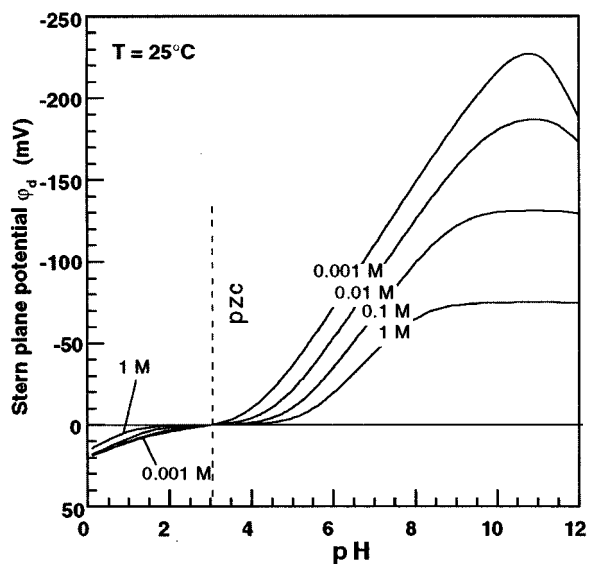
FIG. 3. Stern plane potential φ_d (mV) versus pH at $T=25\,°C$ for different electrolyte concentrations. The ''pzc'' is the point of zero charge of the silica surface, which corresponds also to a zero Stern plane potential condition.

Q_S^0 has been computed from Eq. (103) (recall that $Q_S^0 = -Q_S$). Q_S^0 versus pH is given in Fig. 4 for different electrolyte concentrations. Figure 5 is a graph of Q_S^0 versus the electrolyte concentration at pH=7, 8, and 9. The fractional occupancies of surface sites and ions in the EDL can now be deduced from the knowledge of the Stern plane potential using Eqs. (96) to (99) and their behavior as a function of pH and electrolyte concentration are plotted in Figs. 6 and 7.
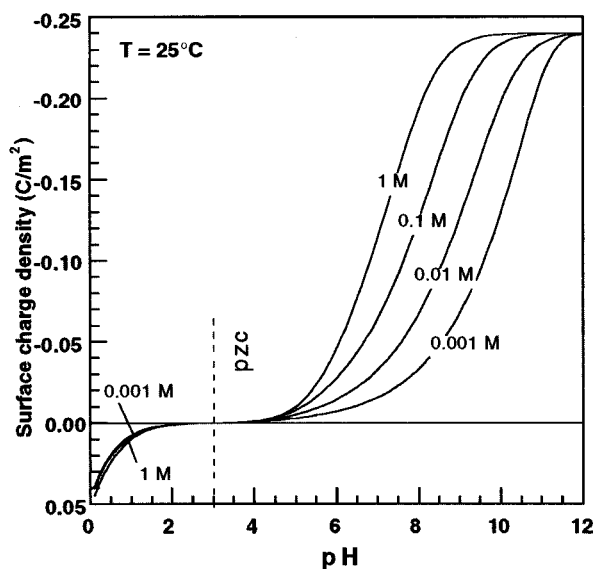
FIG. 4. Surface charge density Q_0^S (C m^{-2}) versus pH for different electrolyte concentrations ($T=25\,°C$). The ''pzc'' is the point of zero charge of the silica surface. The maximum surface charge density is here ±0.240 C m^{-2}, which corresponds to 1.5 charged site nm^{-2}.
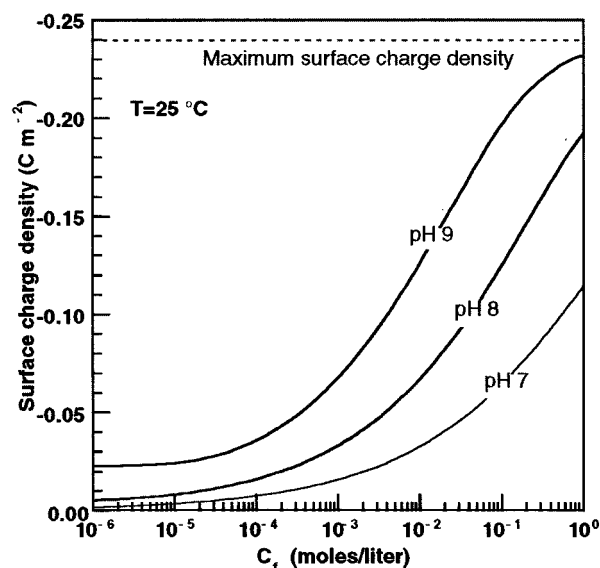

FIG. 5. Surface charge density Q_0^S (C m^{-2}) versus electrolyte concentration (mole/liter) at pH=7 and $T=25\,°C$. Recall that the maximum surface charge is ±0.240 C m^{-2} ($K_{(-)}=10^{-6.3}$, surface site density of 1.5 sites nm^{-2}).

V. DISCUSSION

A. Concerning fractional ionic and surface occupancies

The fractional occupancies of ions in the diffuse layer on a quartz surface given by Eqs. (96) to (99) can be represented by parametric diagrams for each species as done by Glover et al.,[14] (Fig. 7). Referring to Fig. 6, from pH 5 upwards, an increasingly significant part of the surface consists of negative $>$Si-O$^-$ sites. Positive sites are excluded from the surface in this pH domain. In Fig. 6(b), we compare the values from the present theory with the data of Brady (see Ref. 12), which are based on potentiometric titration of SiO$_2$ surfaces at 25 °C. As the pH decreases, the EDL becomes occupied by a continued decreasing number of Na$^+$ ions and an increasing number of H$^+$ ions. Between pH 4.5 and pH 3 the nature of the surface changes with neutral sites replacing the $>$Si-O$^-$. At pH=pH(pzc), the surface is occupied, almost exclusively, by neutral sites, with equal numbers of what few positive and negative surface sites exist. For pH 2–4, the surface charge, the Stern plane potential and the surface conductivity must be very low as the result of the high neutral site occupancy (e.g., Figs. 3 and 4). At progressively lower pH values, the surface becomes positively charged due to the replacement of neutral surface sites, $>$Si-OH, by positive $>$Si-OH$_2^+$ sites (Fig. 6) and the diffuse layer contains H$^+$, Cl$^-$, and Na$^+$ in comparable proportions. Near the PZC, the fractional occupancy of Cl$^-$ ions is relatively insensitive to changes in electrolyte concentration. As mentioned before by Glover et al.,[14] there is little competition between Cl$^-$ and OH$^-$ ions. This is because the availability of OH$^-$ in the solution is always small at those values of pH for which positive charged surface sites exist in significant quantity.

In Fig. 7, results for the fractional ionic occupancies as a function of pH and electrolyte concentration are compared to the results of ISCOM I. ISCOM I (Ref. 14) does not account for a neutral surface site density. It is clear from Fig. 7 that
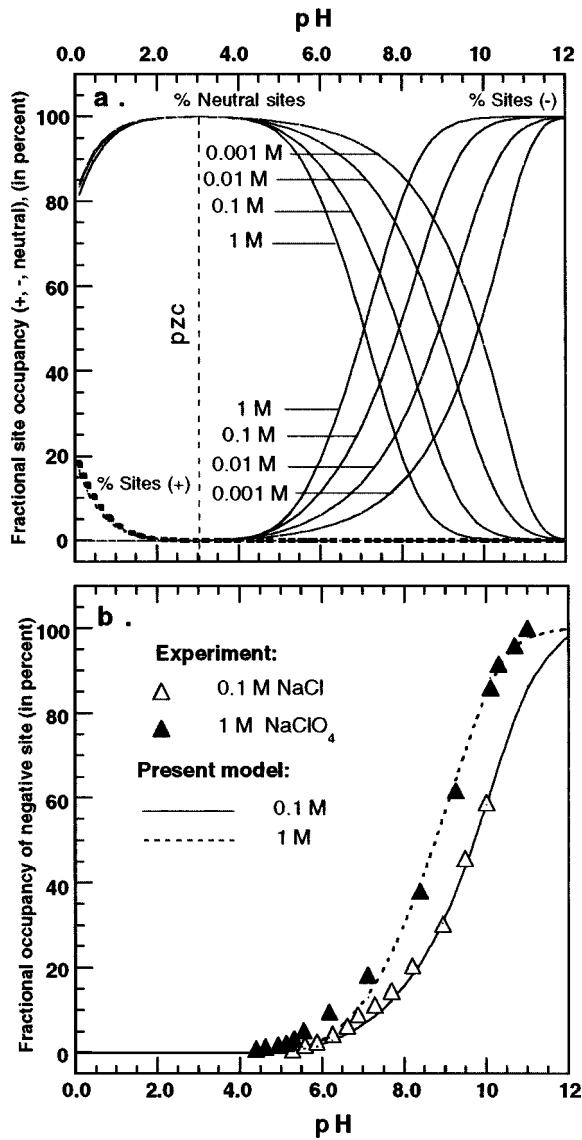
FIG. 6. (a) Fractional site occupancies (in percent) as a function of pH and electrolyte concentration (moles/liter), [$T=25\,°C$, pH(pzc)$=3$, $K_{(-)}=10^{-6.3}$, 1.5 sites nm^{-2}]; (b) comparison with the experimental results of Brady (Ref. 12). Curves are the result of the present model (surface site density: 1.00 mol/kg, $K_{(-)}=10^{-7.5}$).

this leads to an important error in the derivation of EDL occupancies. This is, perhaps, the most important difference between the two models and shows the utility of using three or five site models (this theory) rather than a two-site model (ISCOM I) without EDL description. Clearly, in the application of this theory to any mineral it is important to understand the mechanisms of charged and neutral surface site formation prior to modeling.

B. Concerning Stern plane potential and surface charge density

The variation of the Stern plane potential with the pH and the electrolyte concentration is given in Fig. 3. In practice, the Stern plane potential is not measurable experimentally, however the shear plane potential ζ, for example, determined
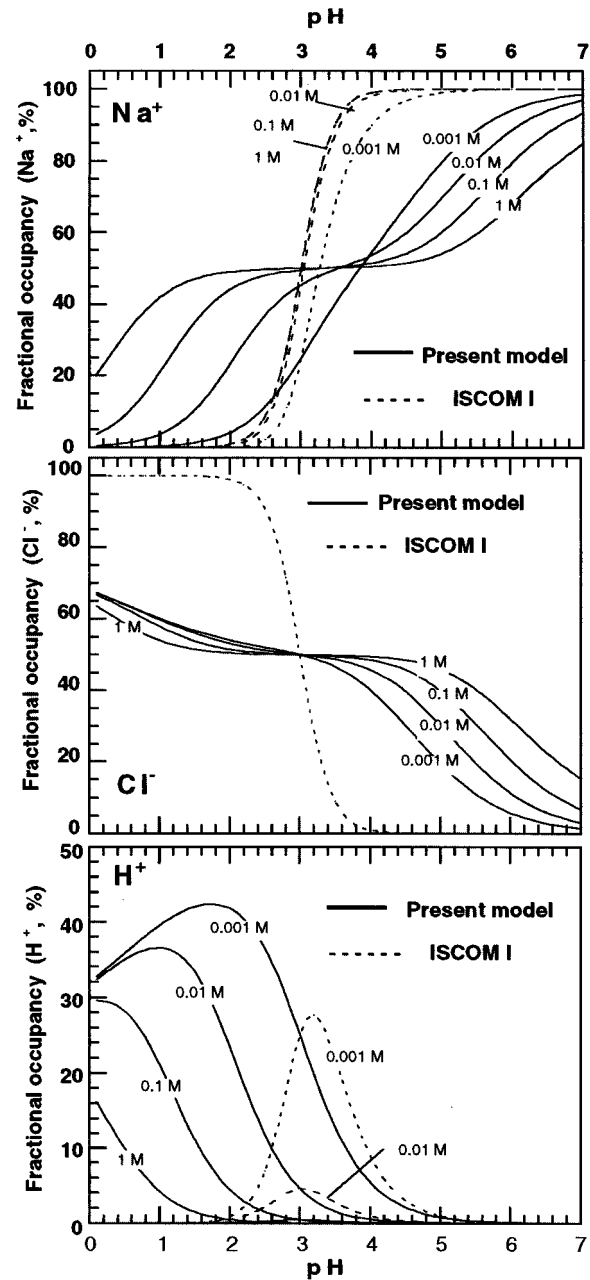

FIG. 7. Fractional ionic occupancies (in percent) in the diffuse layer (present model) and fractional ionic occupancies of adsorbed surface ions (ISCOM I) as a function of electrolyte concentration (NaCl, in moles/liter) and pH for a quartz surface [pH(pzc)$=3$]. The fractional occupancies of hydroxyl ions are not represented in this figure because they are very small compared to the fractional occupancies of the other ions. In ISCOM I, the curves for the surface occupancy of chloride ions are almost identical for all concentrations. At pH 7, the electrical diffuse layer is dominated by sodium ions, however the chloride ions concentration is not negligible.

by a streaming potential method, gives an indication of the variation of φ_d with ionic concentration,[17,22] the pH, and the temperature. Electrokinetic phenomena derive from the relative motion between a charged surface and its associated double layer. The ζ potential is the electrical potential at the slipping plane or shear plane (i.e., the potential within the double layer at the zero velocity surface). Although the ζ
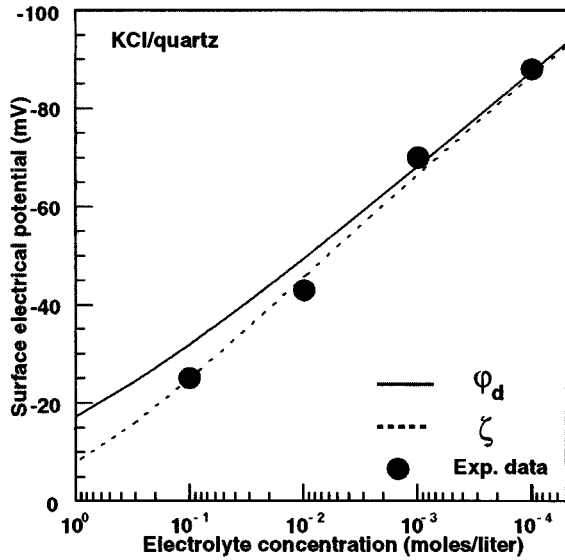
FIG. 8. Zeta and Stern plane potentials (mV) versus electrolyte concentration (moles/liter). Experimental data are from Scales, Grieser, and Healy (Ref. 23) (fused silica, $T = 20 \pm 1$ °C, pH $= 5.8 \pm 1$, KCl electrolyte). The heavy line and the dotted line are theory for the φ_d potential and the ζ potential, respectively (parameters used pH=5.9, 1.5 sites/nm^2, K$_{(-)} = 10^{-6.3}$, pH(pzc)=3, $\chi_\zeta = 2.4$ Å).

potential is undoubtedly an important parameter, there is a problem knowing the location of the shear plane from the surface. We define this distance as χ_ζ, and therefore $\zeta \equiv \varphi(\chi_\zeta) \approx \varphi_d \exp(-\chi_\zeta / \chi_d)$. In Fig. 8, the Stern plane potential and the ζ potential are plotted against the electrolyte concentration together with some experimental data for a quartz-KCl system.[23] Because we have no information about the exact value of χ_ζ, we use χ_ζ as an adjustable parameter and choose its value so that the theoretical ζ-pH relationship fits the experimental data (Fig. 8).

C. Concerning surface conduction

In Fig. 9, the specific surface conductance is estimated for pH 7, 8, and 10, and for electrolyte concentration between $10^{-5} - 1$ mol l^{-1}. The specific surface conductance decreases at high salinity $(0.1 - 1$ mol l$^{-1})$ due to the increase of the electrolyte conductivity. At low salinity, i.e., the second term of Eq. (55) becomes negligible, and consequently the specific surface conductance depends indirectly of the mineral surface charge density, Q_S^0, which decreases when the electrolyte concentration decreases (Fig. 5). The result of these remarks is that we can say, heuristically, that when the surface is not completely saturated with negative sites the specific surface conductance (and therefore the surface conduction) should be very low at very low electrolyte concentrations, as well as at high electrolyte concentrations, with a peak in surface conduction occurring $0.1 - 1$ moles/liter depending on the surface site density (Fig. 9). Note that surface conduction in quartz is low at pH 7 due to a significant fraction of sites being neutral at this pH. In Fig. 10, we plot the effective electrical conductivity as a function of the electrolyte conductivity in a log-log diagram. The difference
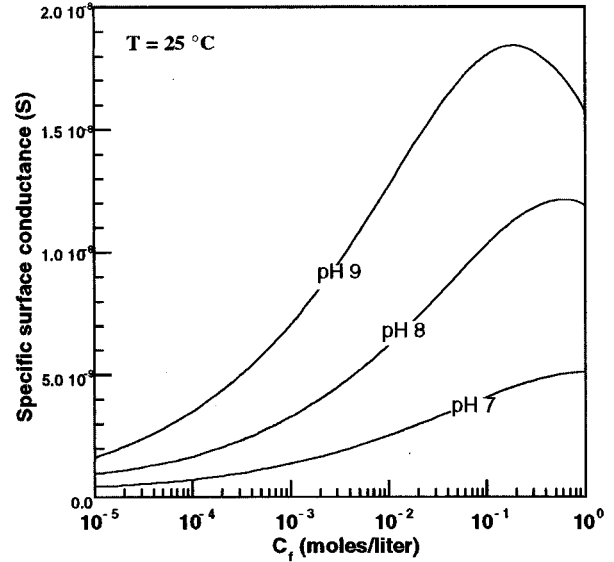

FIG. 9. Specific surface conductance (S) versus electrolyte concentration (moles/liter) at pH 7, 8, and 9, and $T = 25$ °C.

between the case where all the surface is ionized and the prediction of the present model for a quartz sample is more than one order of magnitude at low salinity.

VI. CONCLUSIONS

In this work, we were interested in porous media in which electrical transport is associated with bulk electrical conduction in the pore fluid and surface electrical conduction occurring in the electrical diffuse layer close to the pore-mineral interface. Our model is restricted to the case in which the electrical diffuse layer thickness is small compared to (a) the
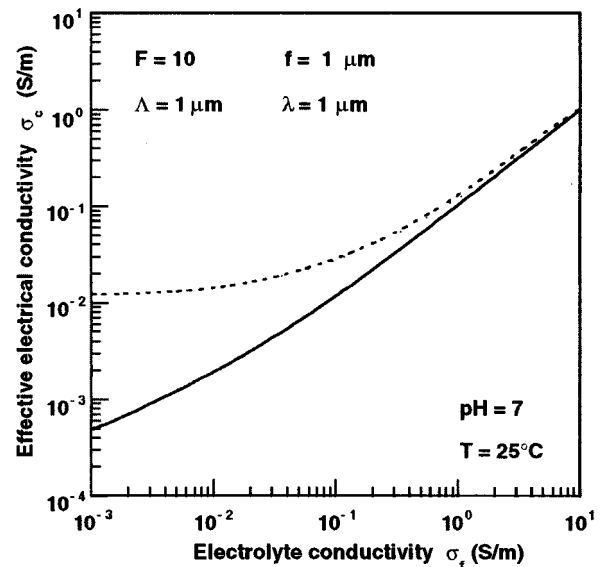

FIG. 10. Effective electrical conductivity σ_c (S/m) versus electrolyte conductivity σ_f (S/m). The dotted line is the relationship given with a negatively saturated surface (all sites are negative), whereas the line is the computation following the present model.

local radius of curvature of the mineral surface, and (b) the pore size (flat and thin electrical diffuse layer), but greater than the average distance between charged sites. In such a system, the relationship between the effective conductivity, σ_c, and the free electrolyte conductivity, σ_f, is nonlinear due to (1) intrinsic geometrical effects, and (2) the variation of the surface charge with the salinity. If specific adsorption effects can be neglected, the model used to describe surface conduction needs only three input parameters for quartz: the surface site density Γ_S^0, and the acid-base equilibrium constants of the surface reactions $K_{(\pm)}$. Each additional specific process of adsorbtion requires the addition of one more parameter (the respective equilibrium constant). The comparison of the results of this paper with a large experimental dataset will be examined in a future work.

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APPENDIX A: MICROSTRUCTURAL PARAMETERS

One way to introduce the JPK microstructural parameters is to present the canonical problem in electrical conductivity.[3] In the present analysis of this paper, this problem should be consider as a conceptual one. Consider electrical conduction in a porous medium saturated by a purely conducting fluid (σ_f is the fluid conductivity) and having an insulating matrix. We consider also that there is an additional surface conductivity, Σ_S, which coats the pore walls. We want to determine the effective conductivity of the porous medium. The analytical solution of this problem is given by Johnson, Plona, and Kojima,[3] and has been studied numerically for special microstructural cases by Schwartz et al.,[3] and Bernabé and Revil.[5]

First, we consider that the fluid conductivity in the interconnected pore space is a function $\sigma(\mathbf{r})$ of position. By equating the macroscopic Joule dissipation to the sum of the electrical local dissipations in the pore space, we have[3,5]

$$\sigma_c = \frac{L^2}{|\Delta\Psi|^2} \int_{V_p} \sigma(\mathbf{r})|\nabla\psi(\mathbf{r})|^2 dV_p, \qquad (A1)$$

where $\Delta\Psi$ and L have been defined in Sec. II A. For the special case where the electrical conductivity is uniform $\sigma(\mathbf{r}) = \sigma_f$, and $\psi(\mathbf{r}) = \psi_b(\mathbf{r})$, the effective electrical conductivity can be written by $\sigma_c = \sigma_f/F$, where F is the first of the four microstructural parameters used by JPK to model transport properties in porous media. The pore volume formation factor, F, is defined by[3-5]

$$\frac{1}{F} \equiv \frac{1}{V} \int_{V_p} |e_b(\mathbf{r})|^2 dV_p, \qquad (A2)$$

where $e_b(\mathbf{r}) \equiv -(L/|\Delta\Psi|)\nabla\psi_b(\mathbf{r})$, and the differential dV_p denotes integration over the interconnected pore space. The pore space formation factor is related to the pore space tor-

tuosity by $\tau_V^2 = F\phi$. If conduction is dominated by pore fluid, with the surface conductivity as a weak perturbation, the effective conductivity is given by[3]

$$\sigma_c = \frac{1}{F}\left(\sigma_f + \frac{2}{\Lambda}\Sigma_S\right). \qquad (A3)$$

The parameter Λ is rigorously related to the local potential distribution $\psi_b(\mathbf{r})$ by[3-5]

$$\frac{2}{\Lambda} \equiv \frac{\int|\mathbf{e}_b|^2 dS}{\int|\mathbf{e}_b|^2 dV_p}, \qquad (A4)$$

where the differential dS denotes integration over the interconnected pore surface. Note that Λ can be viewed as a weighted version of the length parameter V_p/S.[3-5] Λ is the second microstructural parameter introduced by JPK. In the high salinity limit, Eq. (A3) is exact to the first order in perturbation due to surface electrical conduction.[3] The opposite limit, where conduction is dominated by the surface conductivity, is formally similar (in this description) to that given for the high salinity case. The effective conductivity is written in this limit by[3,5]

$$\sigma_c = \frac{1}{f}\left(\Sigma_S + \frac{\lambda}{2}\sigma_f\right), \qquad (A5)$$

which contains the final two microstructural parameters, f and λ. These parameters are rigorously related to the electrical potential distribution, $\psi_S(\mathbf{r})$, that would exist in the absence of bulk fluid conductivity

$$\frac{1}{f} = \frac{1}{V}\int|\mathbf{e}_S|^2 dS, \qquad (A6)$$

$$\frac{2}{\lambda} = \frac{\int|\mathbf{e}_S|^2 dS}{\int|\mathbf{e}_S|^2 dV_p}, \qquad (A7)$$

where $\mathbf{e}_S(\mathbf{r}) = -(L/|\Delta\Psi|)\nabla\psi_S(\mathbf{r})$ (and we have $|\langle\mathbf{e}_S\rangle| = 1$). The surface formation factor, f, is related to the surface tortuosity by $\tau_S^2 = f\phi(S/V_p)$ (note that f has the dimension of a length). The parameters Λ, and λ, are the characteristic dimensions associated with pore and surface transport, respectively. An application of the mathematical Cauchy-Schwartz inequality together with the definitions of F and f leads directly to

$$F \geq \frac{1}{\phi} \quad \text{and} \quad f \geq \frac{V_p}{S}\frac{1}{\phi}, \qquad (A8)$$

where $\phi \equiv V_p/V$ is the interconnected porosity. Electrical conduction minimizes the Joule energy dissipation, and consequently,

$$\int \Sigma_S|\nabla\psi_b|^2 dS \geq \int \Sigma_S|\nabla\psi_S|^2 dS, \qquad (A9)$$

$$\int \sigma_f|\nabla\psi_S|^2 dV_p \geq \int \sigma_f|\nabla\psi_b|^2 dV_p. \qquad (A10)$$

It follows from the definitions of the four microstructural parameters introduced by JPK, and because the specific surface conductance and the electrolyte conductivity are taken independent of position, that

$$\frac{\lambda}{2f} \geq \frac{1}{F} \quad \text{and} \quad \frac{2}{F\Lambda} \geq \frac{1}{f} \qquad (A11)$$

(and consequently, $\lambda \geq \Lambda$).

APPENDIX B: ISCOM I ANALYSIS

We demonstrate here that the model of Glover et al.,[14] ISCOM I, assumes the Nernst relationship between the Stern plane potential, φ_d, and the pH. In ISCOM I we have $\varphi(\chi) \rightarrow \varphi_d$, and therefore the fractional occupancy of H^+ ions in the EDL, $\Omega_{H^+}^S$, is not defined by Eq. (94), but by the following equation:

$$\Omega_i^{S,\text{ISC}} \equiv C_i^S(0) / \sum_j C_j^S(0), \tag{B1}$$

where $C_i^S(0)$ is the ionic concentration of species i at the surface (i.e., for $\chi = 0$). Consequently using the Boltzmann distribution given by Eq. (34), $\Omega_{H^+}^{0,\text{ISC}}$ is equal to

$$\Omega_{H^+}^{S,\text{ISC}} = \frac{10^{-\text{pH}} e^{\widetilde{\varphi}_d}}{2(C_f + 10^{-\text{pH}})(\cosh\widetilde{\varphi}_d)}. \tag{B2}$$

where $\widetilde{\varphi}_d \equiv -e\varphi_d / k_B T$. Note the factor of 2 in the denominator of $\widetilde{\varphi}_d$ in Eq. (96), due to the integration over the total thickness of the diffuse layer, disappears in this last expression. In ISCOM I, $\Omega_{H^+}^{S,\text{ISC}}$ is also given by Eq. (111), so by equating these two relationships, we have, after some algebraic manipulations,

$$\varphi_d = \frac{k_B T}{e} \ln\left(\frac{1}{\Omega_{(-)}^{0,\text{ISC}}} - 1\right)^{1/2}. \tag{B3}$$

Now using Eq. (108) for $\Omega_{(-)}^{0,\text{ISC}}$ together with Eq. (77) for the PZC, inside this last relationship, gives, after some algebraic manipulations, the classical Nernst equation between the pH and the Stern plane potential,

$$\Delta\text{pH} = -\frac{1}{2.303}\left(\frac{e}{k_B T}\varphi_d\right), \tag{B4}$$

where $\Delta\text{pH} \equiv \text{pH} - \text{pH(pzc)}$. Equation (34) can be compared directly with Eq. (93). For oxides of the amphoteric metals Al, Si, and Ti, it is well known that the Nernst equation is not able to account for (1) the observed change of the ζ potential of 26 mV per tenfold change in the electrolyte concentration of a 1:1 univalent electrolyte (Pride and Morgan, Ref. 7 for quartz), and (2) the observation that potentiometric titrations of the surface charge show a strong dependence on electrolyte concentration (Perram, Ref. 20).

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