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Modelling of pH-dependent electro-osmotic flows

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Abstract

NaCl-water saturated kaolinite is observed to show pH-dependent electro-osmotic flow. This behaviour is modelled by computing the electro-osmotic flow between parallel planes as a function of their electrical surface charge density. The latter can be related to pH through the physico-chemical properties of the material. In case of kaolinite particles, isomorphic substitution and two surface dissociation reactions allow to predict the pH-dependence of the electrical charge density and thus the variations of electro-osmotic flows with pH. ***To cite this article: P. Dangla et al., C. R. Mecanique 332 (2004).***
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Résumé

Modélisation des variations de flux électro-osmotiques avec le pH. On étudie l'écoulement électro-osmotique entre deux plaques en fonction de la densité de charge qu'elles portent. Par ailleurs, une modélisation des réactions de dissociation en surface du cristal de kaolinite permet de représenter la variation de cette densité de charge avec le pH. Ces résultats combinés permettent de modéliser les variations des flux électro-osmotiques avec le pH. ***Pour citer cet article : P. Dangla et al., C. R. Mecanique 332 (2004).***
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Version française abrégée

Les flux électro-osmotiques dans les argiles varient avec le pH de la solution interstitielle. Cette dépendance vient des propriétés physico-chimiques du cristal d'argile et en particulier des réactions de dissociation à sa surface qui déterminent, en fonction du pH, la valeur de la densité de charge. Nous nous proposons de modéliser ce phénomène. Pour cela on calcule l'écoulement d'un électrolyte visqueux entre deux plans chargés électriquement et soumis à un champ électrique extérieur E. L'électrolyte porte une distribution de charge, de signe opposé à celui des plans, déterminée par la loi de Boltzmann (6). Le fluide est donc soumis en tout point aux forces de Coulomb résultant de cette distribution de charge et du potentiel électrique local somme du potentiel extérieur $-Ex$ et du potentiel local ψ solution de l'équation de Poisson (1). On recherche une solution stationnaire en vitesse de l'équation générale du mouvement (2). Cette solution, donnée par (5), est la somme d'un terme d'écoulement de Poiseuille classique et d'un terme d'écoulement électro-osmotique fonction du potentiel électrique ψ. Ce potentiel électrique est solution de l'équation de Poisson–Boltzmann (7). Cette solution est calculée numériquement. On peut montrer qu'elle dépend essentiellement de deux nombres sans dimension : $\bar{\sigma}$ traduisant l'intensité de la densité de charge par rapport aux propriétés diélectriques du fluide et $\bar{h}$ le rapport de la demi-distance entre les deux plans et de l'épaisseur de la double couche diffuse. La variation du flux électro-osmotique en fonction de ces deux nombres sans dimension est représentée sur les Fig. 1(a) et (b). La densité de charge à la surface du cristal de kaolinite est la somme d'un terme constant et d'un terme variable dépendant du pH. La charge variable provient des réactions de dissociation des groupes ionisables situés sur les faces latérales et basales de la particule (11). À l'aide des constantes d'équilibre de ces réactions on peut exprimer le pH en fonction de la charge variable et du potentiel électrique de surface (14). Ce potentiel de surface dépend lui-même de la charge totale de surface suivant une relation qui peut être proposée à partir de l'étude précédente. La relation entre le nombre $\bar{\sigma}$ et le pH pour différentes valeurs de $\bar{h}$ est représentée sur la Fig. 2(a). On y voit que cette relation ne dépend quasiment plus de $\bar{h}$ dès que $\bar{h} > 1$ ce qui est pratiquement toujours le cas. Il est alors possible de représenter la variation du flux électro-osmotique en fonction du pH (Fig. 2(b)).

1. Introduction

Electro-osmotic properties of clays result from the existence of electrical surface charge on the solid particles of clays. Part of this surface charge arises from reactions occurring between the ionisable surface groups located at the solid surface of the clay particle and the ions present in the aqueous solution. As a result the surface charge together with the electro-osmotic flows are pH-dependent. This Note deals with the modelling of this phenomenon. To do so the problem of electro-osmotic flow between two electrically charged planes is considered. This result has already been formulated in a cylindrical capillary by Rice and Whitehead [1]. However, all these relationships involve the assumption that the electric potential is small (compared to $k_B T/e$). Unfortunately this assumption, known as the Debye–Hückel approximation, is not fulfilled for the material studied here. Hence in the following section a numerical solution of the problem is given and studied with various parameters. In the third section the variations of the surface charge is computed against the pH by applying a model of dissociation reactions [2,3]. Combining these results provides a model to determine the variations of electro-osmotic properties with pH.

2. Electo-osmosis between two charged planes

Let us consider a symmetric electrolyte of ionic charge number Z and bulk ionic concentration n_0 ions/unit volume. The planes, separated at distance $2h$, carry a surface charge σ. Furthermore the whole system is placed in a uniform external electric field E. The directions of the field and the planes are parallel to x-axis and perpendicular to z-axis. At any point of the electrolyte, the electric potential ϕ is then the sum of the external potential $-Ex$ and

the electric double layer potential $\psi(z)$ resulting from the surface charge and the ions: $\phi(x, z) = \psi(z) - Ex$. If the excess charge density is $q(z)$, then the Poisson equation has the form

$$\frac{d^2\psi}{dz^2} = -\frac{q}{\epsilon} \tag{1}$$

In this equation ϵ is the permittivity which is assumed to be uniform throughout the liquid. Let us now establish the velocity of the fluid due to a uniform applied pressure gradient and the body force caused by the action of the applied electric field on the net charge density $q(z)$. The basic equation of motion for the fluid is

$$-\underline{\nabla p} + \mu \Delta \underline{v} + \underline{f} = \rho \left(\frac{\partial \underline{v}}{\partial t} + \underline{\underline{\nabla v}} \cdot \underline{v} \right) \tag{2}$$

with div $\underline{v} = 0$ as the fluid is incompressible. In this equation ρ is the mass density, μ is the coefficient of viscosity and $\underline{f}$ is the body force per unit volume due to the electric field, namely $\underline{f} = -q\underline{\nabla\phi}$. Let us look for a stationary solution of the form $\underline{v} = v(z)\underline{e_x}$. In this case the inertia terms vanish. The previous equation thus reduces to

$$\frac{\partial p}{\partial z} + q \frac{d\psi}{dz} = 0 \qquad -\frac{\partial p}{\partial x} + \mu \frac{d^2 v}{dz^2} + q E = 0 \tag{3}$$

Substituting expression (1) for q in these equations, using the boundary condition $v(h) = 0$ and the symmetry conditions $\frac{dv}{dz}(0) = \frac{d\psi}{dz}(0) = 0$, the solutions for v and p of the previous equations are found as

$$p(x, z) = p_0(x) + \frac{\epsilon}{2} \left(\frac{d\psi}{dz} \right)^2 \tag{4}$$

$$v(z) = -\frac{1}{2\mu} \frac{dp_0}{dx} (h^2 - z^2) + \frac{\epsilon}{\mu} E \big(\psi(z) - \psi(h) \big) \tag{5}$$

The velocity is then the sum of a Poiseuille flow term and an electro-osmotic term determined by the electric double layer potential ψ. Let us now determine this potential. From the Boltzmann equation

$$q = -2Zen_0 \sinh \frac{Ze\psi(z)}{k_B T} \tag{6}$$

In this equation k_B is the Boltzmann constant (1.38×10^{-23} J/K), e is the electronic charge (1.6×10^{-19} C) and T the temperature. At room temperature $k_B T/e \approx 25$ mV. So for univalent ions, the Debye–Hückel approximation would be valid only for $\psi \ll 25$ mV. Below it will be shown that this condition does not hold. The Poisson–Boltzmann equation results from the combination of (1) and (6):

$$\frac{d^2\psi}{dz^2} = \frac{2Zen_0}{\epsilon} \sinh \frac{Ze\psi(z)}{k_B T} \tag{7}$$

One of the boundary condition has already been mentioned and expresses the symmetry condition at the midplane. The second boundary condition follows from the requirement of overall electroneutrality i.e. $\int_0^h q \, dz + \sigma = 0$. Substituting (1) in this equation yields the second boundary condition at the wall under the form $\frac{d\psi}{dz}(h) = \frac{\sigma}{\epsilon}$. Using these boundary conditions, the general solution of (7) is found numerically. However, writing $\psi(z) = \frac{k_B T}{Ze} \bar{\psi}(\bar{z})$ with $\bar{z} = \frac{z}{h}$ shows that $\bar{\psi}(\bar{z})$ only depends on two dimensionless parameters: $\bar{\sigma} = \sigma/\sqrt{2k_B T \epsilon n_0}$ and $\bar{h} = \kappa h$ where $\kappa^{-1} = \sqrt{k_B T \epsilon/(2Z^2 e^2 n_0)}$ is the double-layer thickness or the Debye length. With $\sigma = -0.2$ C/m^2, $n_0 = 0.01$ mole/l, $Z = 1$, $\epsilon = 80\epsilon_0$, $T = 293$ K, we find $\bar{\sigma} = -34$ and $1/\kappa = 30$ Å. In the following it is assumed that the function $\bar{\psi}(\bar{z})$ is found from the numerical resolution of the previous equations.

Under conditions of no applied pressure gradient, the electro-osmotic velocity is given by

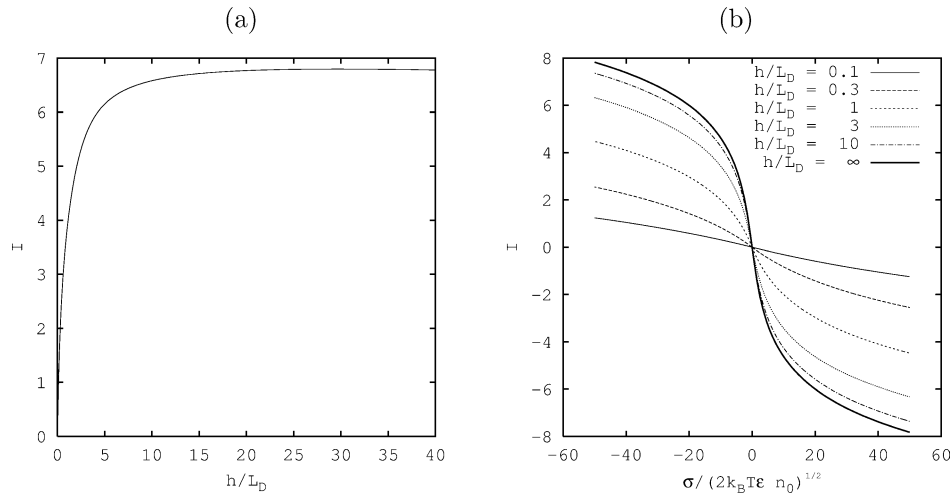$$v(z) = \Omega \big(\bar{\psi}(\bar{z}) - \bar{\psi}(1) \big) E \tag{8}$$

Fig. 1. Integral I as a function of: (a) $\bar{h}$; (b) $\bar{\sigma}$ for various values of $\bar{h}$.

where $\Omega = \frac{k_B T \epsilon}{Z e \mu}$. With the previous values and $\mu = 10^{-3}$ Pa.s we have $\Omega = 1.79 \times 10^{-8}$ m^2/(V.s). For $\bar{h} \gg 1$, asymptotic expansions show that $\bar{\psi}$ is negligible, except in the double layer region very close to the wall where under these conditions $\bar{\psi}(1) = 2\,\mathrm{asinh}\,\frac{\bar{\sigma}}{2}$. Since $\bar{\sigma}$ exceeds generally 2 for current applications, it can be seen easily that the Debye–Hückel approximation does not hold. For $\bar{h} \ll 1$, $\bar{\psi}$ can be approximated by

$$\bar{\psi}(\bar{z}) = -\frac{\bar{\sigma}\bar{h}}{2}(1 - \bar{z}^2) + \mathrm{sgn}(\bar{\sigma}) \ln \frac{2|\bar{\sigma}|}{\bar{h}} \qquad (9)$$

The velocity is thus the same as in Poiseuille flow with an effective pressure gradient equal to $\frac{\sigma e}{2h} E$. The Poiseuille characteristics at low values of $\bar{h}$ are due to the large overlap of the double layers with a quasi constant net charge density across the fluid, this giving rise to a fluid body force similar to that of a pressure gradient.

The electro-osmotic flow Q is obtained by integrating expression (8) for $v(z)$ over a cross section of area $A = 2h$

$$Q = \Omega I E A \qquad I = \int_0^1 \big(\bar{\psi}(\bar{z}) - \bar{\psi}(1)\big)\,d\bar{z} \qquad (10)$$

Integral I is plotted in Fig. 1(a) and (b) against $\bar{h}$ and $\bar{\sigma}$. Fig. 1(a) shows that the greatest change of I with $\bar{h}$ is in the region $0 < \bar{h} < 10$ while I has 90% of its maximum value, namely $-2\,\mathrm{asinh}\,\frac{\bar{\sigma}}{2}$, for $\bar{h} > 20$. This function is plotted in Fig. 1(b) for $\bar{h} = \infty$. According to expression (9), I can be approximated by $-\bar{\sigma}\bar{h}/3$ for $\bar{h} \ll 1$. Fig. 1(b) confirms the linear relationship between I and $\bar{\sigma}$ for pratically $\bar{h} < 0.1$. However, values of $\bar{h} < 1$ are not readily realizable in practice. For instance, an estimation of h following from the relationship $\rho_{sol} S_m h = e$, gives $\bar{h} = 7.9$, where ρ_{sol} is the mass density of the kaolinite crystal, S_m the specific surface and e the void ratio. This value is obtained for $S_m = 15$ m^2/g, $\rho_{sol} = 2.8$ g/cm^3, $e = 1$ and $1/\kappa = 30$ Å [3,4].

3. Modelling of the variations of the surface charge with the pH

The surface charge of kaolinite depends on the pH of the aqueous solution as shown hereafter. There are two types of charge, permanent and variable. Permanent charge arises from isomorphous substitution of cations (for example the substitution of Si^{4+} for Al^{3+}) in the lattice of the crystal of kaolinite [2]. After [5] this permanent

surface charge is small and lies in the range of [1;8] mEq/100g or – [0.064;0.5] C/m^2. The origin of the variable charge is the consequence of the reactions occurring between the ionisable surface groups and the ions present in the aqueous solution. The acid-base properties of these groups (e.g. AlOH) are responsible for the sign of the surface charge and its pH-dependence. This surface charge is positive when in low pH environment (acid) but negative in high pH environement (basic) [3,6]. It vanishes at a pH value denoted by pH_p which, according to some authors, is about 5.5 [7].

Therefore the total surface charge can be expressed as the sum of a permanent charge σ_p and a variable charge σ_v: $\sigma = \sigma_p + \sigma_v$. Let us assume that the variable charge results from the protonation (at low pH) or the deprotonation (at high pH) of amphoteric surface complexes like AlOH [7]:

$$AlOH_2^+ \overset{K_1}{\rightleftharpoons} AlOH + H^+ \qquad AlOH \overset{K_2}{\rightleftharpoons} AlO^- + H^+ \tag{11}$$

Calculating σ_v as a function of pH is classical [2]. The equilibrium constants of the acid-base reactions (11) are defined by:

$$K_1 = \frac{[AlOH][H^+]_s}{[AlOH_2^+]} \qquad K_2 = \frac{[AlO^-][H^+]_s}{[AlOH]} \tag{12}$$

where $[AlOH_2^+]$, $[AlOH]$ and $[AlO^-]$ are surface densities (mol/unit surface area) while $[H^+]_s$ is the molar concentration of protons in the solution in contact with the surface (mol/unit volume). $[H^+]_s$ is given by the Boltzmann equation:

$$[H^+]_s = [H^+]_0 \, e^{-Ze\psi^s/k_BT} \tag{13}$$

where $pH = -\log[H^+]_0$ and ψ^s is the electric potential at the surface of the particle. The total number of surface sites per unit area is $N = [AlOH] + [AlOH_2^+] + [AlO^-]$. Let us denote $\sigma_N = eN$, $s_v = \sigma_v/\sigma_N$, $s_p = \sigma_p/\sigma_N$ and note that $\sigma_v = e([AlOH_2^+] - [AlO^-])$. It is not difficult to show that

$$pH = \log\left[\frac{ab(1-s_v)}{s_v + (s_v^2 + a^2(1-s_v^2))^{1/2}}\right] - 0.43\frac{Ze}{k_BT}\psi^s \tag{14}$$

with $a = \sqrt{4K_2/K_1}$ and $b = 1/\sqrt{K_1K_2}$. In the literature, there is not a general agreement on the values of K_1 and K_2 even for the same material like kaolinite (see for example [7]). So it is more convenient to express a and b in terms of particular values of pH. Let us denote by pH_p and ψ_p^s the pH and the electric potential associated with a null variable charge $s_v = 0$ i.e. $\sigma = \sigma_p$. Then it is easy to show that $\log b = pH_p + 0.43\frac{Ze}{k_BT}\psi_p^s$. Furthermore it is common to introduce the pH at which the total surface charge is zero (point of zero charge), denoted by pH_0. We find $a = -s_p/(\sinh\xi + s_p\cosh\xi)$ where $\xi = 2.3(pH_p - pH_0) + Ze\psi_p^s/k_BT$. After some authors $pH_p = 5.5$ and $pH_0 = 3.5$ for kaolinite [7,8]. These values have been considered hereafter.

As discussed in the previous section the term $Ze\psi^s/k_BT = \bar{\psi}(1)$ depends on $\bar{\sigma}$ and $\bar{h}$. Therefore the relationship (14) allows us to express the pH as a function of $\bar{\sigma}$ and $\bar{h}$. Let us introduce the dimensionless parameters $\bar{\sigma}_N = \sigma_N/\sqrt{2k_BT\epsilon n_0}$ and $\bar{\sigma}_p = \sigma_p/\sqrt{2k_BT\epsilon n_0}$. The function $\bar{\sigma} = f(pH)$ is plotted in Fig. 2(a) for various values of $\bar{h}$. This result is obtained for $N = 0.94$ site/nm^2 ($\bar{\sigma}_N = 25$) and $\sigma_p = -0.015$ C/m^2 ($\bar{\sigma}_p = -2.5$). This figure clearly shows that $\bar{\sigma}$ is practically independent of $\bar{h}$ for $\bar{h} > 1$. Therefore combining the previous results allows us to finally write I as a function of pH. This function, plotted in the Fig. 2(b), is expected to model the variations of the electo-osmotic permeability of kaolinite with the pH. The modelling of the electro-osmotic permeability itself is beyond the scope of this work. Some experimental results are also reported and compared to the theoretical results. Experimental points represent the ratio k_e/Ω where $\Omega = 0.75 \times 10^{-9}$ m^2/(V.s) and k_e is the electro-osmotic permeability found from experiments performed on the same type of material [9].

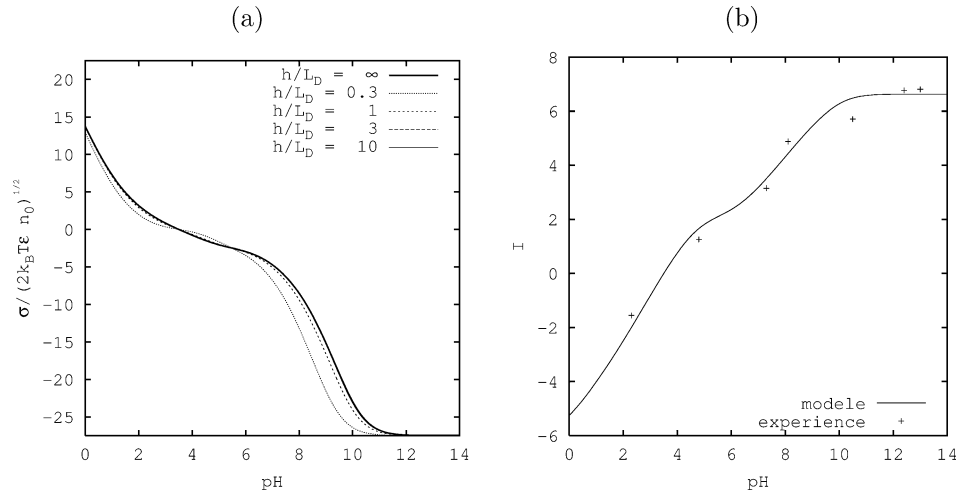(a)   (b)

Fig. 2. $\bar{\sigma}$ (a) and I (b) as a function of pH.

4. Conclusion

The electro-osmotic flow between two charged planes resulting from the application of an electric field has been computed. The dependence of the solution of this problem on the surface charge and the interplane distance has been calculated. Further, a model of dissociation reactions at the surface of the kaolinite particles has been applied to calculate the relationship between the surface charge and the pH of the aqueous solution. Combining these results has allowed us to model the dependence of the electro-osmotic permeability of kaolinite on the pH. These theoretical results qualitatively agree with experiments performed on the same type of materials.

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