Electrolytic Conduction in Porous Media with Charges

Pabitra N. Sen and Rui Kan[(a)]
Schlumberger-Doll Research, Ridgefield, Connecticut 06877

(Received 18 September 1986)

The conductivity of a porous medium made of periodically arranged insulating cylinders with fixed lattice charges is a nonlinear function of the water conductivity via a key dimensionless parameter ξ which is a function of the surface counterion number density, the diffusion coefficient in the double layer, the ion density far from the double layer, and the particle radius. When $\xi \ll 1$, one obtains commonly employed empirical relations.

PACS numbers: 66.10.Ed, 72.60.+g, 73.25.+i, 82.45.+z

Recently, there has been a great deal of interest in electrical conduction in porous media saturated with brine.[1] It has been well known[2] for over 25 years that the composite conductivity σ is a nonlinear function of electrolyte conductivity σ_w when the material contains charged particles like clay particles. In this paper, using a model of a double layer, we explain for the first time,[3] from first principles, this and other related experimental facts which have been of great importance in geophysical exploration.[2] The results obtained here will be applicable to conduction in diverse kinds of porous media: beds of ion-exchange resins, bones, suspension of biological cells, and charged polystyrene balls, to name a few.

We show that the conductivity depends on a key dimensionless parameter $\xi = \Omega_+ r_+ / N_0 a$, that represents the surface effects, where ξ is the surface ion number density Ω_+ times the ratio r_+ of average diffusion coefficient in the double layer divided by that outside, divided by the bulk ion density N_0 far from the double layer times the particle radius a. We will find below that σ is a nonlinear function of ξ and hence of $\sigma_w \equiv \mu_E N_0$. Here μ_E is the mobility of ions.

Conduction in a large class of porous sedimentary rocks takes place through electrolytes which are present in the pores of insulating rock grains. The clay particles are ubiquitous and affect this conductivity because of excess counterions that balance the charge defects fixed in their lattices. In the presence of water these counterions form a cloud called the "double layer" around the clay particle.

In order to understand conduction in porous media with clays, consider a periodic array of charged cylinders immersed in a simple electrolyte like NaCl solution. The cylinders have immobile negative charges in the lattice that are balanced by mobile counterions that reside in the double layer with an effective surface ion number density Ω_+. We assume the Gouy-Chapman model[4,5] where the ion densities are given by $N_\pm = N_0 \exp(\mp \Psi)$, for positive and negative species with charges $\pm e$, and N_0 is the density of the positive and negative ions in the bulk—far from the surface. Here we made the potentials nondimensional by multiplying by $e/k_B T$. The charges and potentials fall off exponentially over the Debye screening distance $\delta = (\varepsilon'_w k_B T / 2e^2 N_0)^{1/2}$, where k_B is the Boltzmann constant, T is the temperature, and ε'_w is the real part of dc dielectric constant of the electrolyte.

The equations in the presence of the external field are linearized with respect to the applied electric field E_{ex} and the currents are given as

$$\begin{aligned} \mathbf{j}_\pm &= -N_\pm D_\pm \nabla \mu_\pm \\ &= -D_\pm (\nabla n_\pm \pm N_\pm \nabla \psi \pm n_\pm \nabla \Psi), \qquad (1) \\ \nabla \cdot \mathbf{j}_\pm &= 0. \end{aligned}$$

Here, following Fixman,[4] we define chemical potentials,

$$\mu_\pm = n_\pm / N_\pm \pm \psi. \qquad (2)$$

The upper case denotes quantities prior to the application of the external electric field; and the lower case, the changes due to the external field.

Outside the double layer, the Debye shielding makes Ψ exponentially small and $N_\pm = N_0$, and for thin double layer $\delta \to 0$ and we find[5]

$$\nabla^2 \psi = 0, \quad \nabla^2 n_\pm = 0, \quad n_+ = n_-. \qquad (3)$$

The Fixman boundary conditions, which relate quantities just outside of the double layer, are obtained by our integrating the continuity Eq. (1) over the double layer and making a physical approximation that the tangential component of the gradient of the chemical potential is independent of the distance from the particle surface. For a cylinder of radius a, this gives

$$\partial \mu_\pm / \partial r + (\Omega_\pm r_\pm / N_0 a^2) \partial^2 \mu_\pm / \partial \theta^2 = 0. \qquad (4)$$

The above approximation has been justified by Chew[5] and can be shown[6] to be an excellent one for the range of ξ used here. For very high values of ξ this boundary condition breaks down. In Eq. (4) $\Omega_- = 0$, and r_+ is obtained by the following averaging:

$$\Omega_+ r_+ = \frac{\int_a^{a+\delta} N_+(r) D_+(r)\, dr}{D_+(\text{outside double layer})}. \qquad (5)$$

Next we consider a square array of cylinders with a cell size of α and the porosity $\phi = 1 - \pi a^2 / \alpha^2$. We follow Lord Rayleigh,[7] and expand the potential and ion densities around a single cylinder as follows:

$$\psi = A_0 + \sum_{n=1} (A_n r^n + B_n r^{-n}) \cos n\theta, \quad r > a+\delta, \tag{6}$$

$$n_\pm = D_0 + \sum_{n=1} (D_n r^n + E_n r^{-n}) \cos n\theta, \quad r > a+\delta. \tag{7}$$

For each n we have four unknowns A_n, B_n, D_n, E_n. For a periodic system, all the coefficients are identical from cell to cell. The solutions which grow with r around one cylinder are equal to the sum of decaying solutions from all other cylinders, and this gives two sets of relations among the unknown coefficients. The other two sets of relations follow from Eq. (4).

The conductivity is computed by Rayleigh's technique[7] which uses Green's theorem $\int ds\,(U\partial\psi/\partial n - \psi\partial U/\partial n) = 0$, where $U = r\cos\theta$. Choose the contour of integration over ds as the perimeter of the unit cell *and* a circle of radius $a+\delta+0^+$. In this region, U and ψ both satisfy Laplace's equation (3). Over those sides of the cell which are parallel to the external field **H**, $\partial\psi/\partial n$ and $\partial U/\partial n$ both vanish. Over the other sides which are perpendicular to the field **H**, $\partial\psi/\partial n$ is proportional to the current entering and leaving the cell but ψ differs by the voltage drop Ha across the cell. Thus we obtain a relation between current and voltage, i.e., the conductivity in terms of the remaining integral over the circle. Over the circle, $U = a\cos\theta$ and $\partial U/\partial n = -\cos\theta$ so that only terms of ψ which are proportional to $\cos\theta$ survive in the integral to give

$$\sigma = \sigma_w (1 - 2\pi B_1 / a^2 H). \tag{8}$$

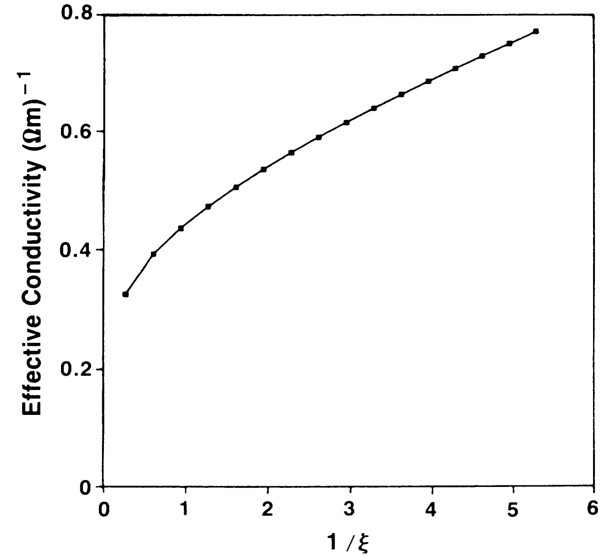

FIG. 1. Effective conductivity as a function of dimensionless scaling variable ξ for $\phi = 0.22$.

It is tedious but straightforward to solve the above equations. O'Brien and Perrins[8] have numerically solved similar equations with similar boundary conditions for fixed porosity and for a limited range of other parameters. Their main goal was to study conductivity as a function of surface (zeta) potential. The work[4,5] on dielectric constant of dilute suspensions (which amounts to solving the above equations for a single particle) contains implicitly the dc conductivity but this was not investigated since the main goal there was to explain the dielectric enhancement. The previous studies did not explore the conductivity problem in the context of the well-known empirical laws[2] and several other experimental facts,[2,9,10] which is our goal here.

To keep terms beyond $n=3$ requires numerical methods, but all the relevant results are obtained by keeping terms up to $n=3$, which we can solve analytically to find

$$\sigma/\sigma_w = 1 + (1/F - 1)G(\xi,\phi), \tag{9}$$

$$G(\xi,\phi) = \frac{(1+3\xi) + (1-\phi)(1-\xi)(1+3\xi)(S_2/\pi) + (1-\phi)^4(-6\xi^2+\xi-3)S_4^2/\pi^4}{(1+\xi)(1+3\xi) + (1-\phi)(1-\xi)(1+3\xi)(S_2/\pi) + (1-\phi)^4(-9\xi^2+12\xi-3)S_4^2/\pi^4}.$$

Here, S_n are lattice-structure factors, and Rayleigh[7] gave their values as $S_2 = \pi$, $S_4 = \pi^4 \times 0.03235$, etc., and F is the formation factor in absence of charge, given by Eq. (10) below. In the limit of uncharged particles $\xi = 0$, Eq. (9) becomes

$$\sigma(\xi=0)/\sigma_w \equiv 1/F = 1 - 2(1-\phi)/[1 + (1-\phi)S_2/\pi - 3(1-\phi)^4 S_4^2/\pi^4]. \tag{10}$$

Equation (9) shows clearly that σ is a nonlinear function of ξ and hence of σ_w. This is illustrated in Fig. 1. Nonlinearity is due to the fact that the conduction paths are not simply two resistors (bulk and double layer) in parallel as assumed in Refs. 2. Because of bending of electric field lines the geometrical factors affecting the double layer region are different from those in bulk and instead of a simple volume average of bulk conductivity and double layer conductivity, we obtain a more complicated formula. These geometrical factors are intertwined with ξ in Eq. (9).

We can demonstrate that the nonlinear behavior is due, in part, to bending of the electric fields[6,11] by a simpler model of a periodic array of *uncharged* insulating spheres coated with a conducting layer, and with brine-saturated pores and no diffusion current. This has been demonstrated both by a numerical simulation[11] and analytically by extending Rayleigh's method for coated spheres.[6] As elementary as this may seem, this simple demonstration was given only recently.

Linear behavior of σ vs σ_w results when $\xi \ll 1$. At high salinity $N_0 \gg 1$ or low surface ion density, or low ionic mobility at the surface, $r_+ \ll 1$, the key parameter becomes small, $\xi \ll 1$. Expanding G to first order in ξ we find

$$G \to 1 - \xi \frac{1 + 11(1-\phi)^4 S_4^2/\pi^4}{1 + (1-\phi)S_2/\pi - 3(1-\phi)^4 S_4^2/\pi^4} = 1 - g\xi, \qquad (11)$$

i.e., $G \approx 1 - g\xi$. Thus the geometrical term and charge terms, which are intertwined in general, factor for small ξ and Eq. (9) simplifies to

$$\sigma = (1/F)[\sigma_w + (F-1)g(\mu_{\rm in}\Omega_+/a)], \qquad (12)$$

where

$$\mu_{\rm in} = r + \mu_E.$$

Equation (12) has a form similar to those obtained empirically.[2] In order to make comparison with empirical relations,[2] we rewrite (12) in terms of Q_v which is the counterion concentration per unit pore volume $Q_v = 2\Omega_+(1-\phi)/a\phi$:

$$\sigma = (1/F)(\sigma_w + AQ_v). \qquad (13)$$

Thus we find a theoretical justification for the empirical relations in the high-salinity range suggesting parallel conduction. But now there are additional geometrical factors which multiply the $\mu_{\rm in}Q_v$ term.

The additional geometrical factors contained in A can explain several other empirical observations. First, for a reasonable value of $\phi \approx 0.2$, Eq. (12) gives the effective counterion mobility $A \approx \mu_E/4 \approx 4$ (S/m) (liter/mole). This value is not far from the value of coefficient multiplying Q_v as deduced by Waxman and Smits[2] in this regime, albeit for real rocks. Second, note that the zero of this linearized Eq. (12) occurs at $C_x = -\sigma_w - AQ_v$, which depends not only on Q_v but also on geometrical factors in A. This explains the scatter observed[2] in C_x vs Q_v plots where different core samples having different porosities and geometries were used in the same plot. Also, the dependence on r_+ is in qualitative accord with experimental data[9,10] where exchanging the counterion Na^+ with less mobile ions such as Ca^{++} reduced the conductivity.

In conclusion, we have explained the nonlinear dependence of σ vs σ_w as well as the empirical linear relations at high σ_w. Our theory is for a two-dimensional periodic array and therefore cannot be used directly on experimental data on real rocks. However, our model gives us enough insight to propose that a correct formulation of the problem should entail the correct scaling variable ξ.

We are grateful to C. Clavier, P. Day, B. Halperin, D. Johnson, A. Sibbit, and S. Whittingham for useful discussions.

---

[a] Present address: Department of Physics, Princeton University, Princeton, NJ 08544.

[1] P. N. Sen, C. Scala, and M. H. Cohen, Geophysics **46**, 781 (1981); D. L. Johnson, T. J. Plona, C. Scala, F. Pasierb, and H. Kojima, Phys. Rev. Lett. **49**, 1840 (1982); G. Milton, in *Physics and Chemistry of Porous Media,* edited by D. L. Johnson and P. N. Sen, AIP Conference Proceedings No. 107 (American Institute of Physics, New York, 1984); P.-z. Wong, J. Koplik, and J. P. Tomanic, Phys. Rev. B **30**, 6606 (1984); J. B. Roberts and L. M. Schwartz, Phys. Rev. B **31**, 5990 (1985); A. J. Katz and A. H. Thompson, Phys. Rev. Lett. **54**, 1325 (1985); B. I. Halperin, S. Feng, and P. N. Sen, Phys. Rev. Lett. **54**, 2391 (1985); S. A. Trugman, Phys. Rev. Lett. **57**, 610 (1986).

[2] M. H. Waxman and L. J. M. Smits, SPE J. **8**, 107 (1968); C. Clavier, G. Coats, and J. Dumanoir, SPE J. **24**, 153 (1984).

[3] A plot showing nonlinear behavior of σ vs σ_w for a 3D periodic array was recently sent to P. N. Sen by R. W. O'Brien, private communication.

[4] M. Fixman, J. Chem. Phys. **72**, 5177 (1980), and **78**, 1483 (1983).

[5] W. C. Chew and P. N. Sen, J. Chem. Phys. **77**, 2042 (1982); W. C. Chew, J. Chem. Phys. **80**, 4541 (1984); W. C. Chew and P. N. Sen, in *Proceedings of the Symposium on Chemistry and Physics of Composite Media,* edited by M. Tomkiewicz and P. N. Sen, Vol. 85-8 (Electrochemical Society, Pennington, N.J., 1985), p. 94.

[6] R. Kan and P. N. Sen, unpublished.

[7] Lord Rayleigh, Philos. Mag. **34**, 481 (1892).

[8] R. W. O'Brien and W. T. Perrins, J. Colloid Interface Sci. **99**, 20 (1984).

[9] H. J. Vinegar and M. H. Waxman, in Society of Professional Well Log Analysts 25th Annual Logging Symposium, New Orleans, La., 1984 (unpublished).

[10] A. Sibbit, private communication; S. Whittingham, private communication.

[11] D. L. Johnson, J. Koplik, and L. Schwartz, Phys. Rev. Lett. **57**, 2564 (1986).