A New Equation for Electroosmotic Flow and Its Implications for Porous Media

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A new form of the equation for electroosmotic flow in capillaries has been developed. The equation appears to unify the Helmholtz-Smoluchowski theory, applying to large capillaries with double layers that are thin when compared with the capillary radius, and the Schmid theory, applying to microporous systems with essentially uniform charge distributions. The major advantages of the new equation are simplicity and ability to be used for a wide range of capillary diameters. Analysis of the equation suggests that the electroosmotic velocity of flow in a porous medium such as soil is related to permeability, porosity, pore ion conductivity and soil plasticity properties.

•UNDER the influence of an applied electric field, water will migrate through porous media. Termed electroosmosis, this phenomenon has proven useful in the solution of many engineering problems.

At present only relatively simple theories are available for use in predicting the velocity of water flow during electroosmosis. These theories are mainly based on experiments performed in individual capillary tubes and ignore many important but complicating effects such as those resulting from temperature, ion exchange, and electrolysis as a function of time, surface conductance, nonuniform geometry of capillaries, variable viscosity of the pore fluids, etc. Nevertheless, these theories have proven useful to engineers and scientists.

The discovery of the phenomenon of electroosmosis is credited to Reuss in 1808. Helmholtz (2) proposed the first analytical theory to explain electroosmosis in 1879 and this theory was partially generalized and improved by Smoluchowski (8) in 1921. The Helmholtz-Smoluchowski theory is now considered valid for large capillaries in which the electric double layer is small when compared with the capillary radius. To explain electroosmosis in the special case of very small capillaries (microcapillaries), a theory was presented by Schmid (7) in a series of papers between 1950 and 1952. An attempt to unify the Helmholtz-Smoluchowski and Schmid theories was made by Oel (5) in 1955; however, his equation cannot be integrated when the general case is considered.

The theories of electroosmotic flow are generally referenced to the zeta potential, defined by van Olphen (9) as the "electric potential in the double layer at the interface between a particle which moves in an electric field and the surrounding liquid." It can also be defined as the potential across an equivalent condenser having one plate at the plane of shear in the fluid surrounding the particle and the other some distance away in the mobile part of the electric double layer. A more specific definition of the distance between the plates of the equivalent condenser would be useful in defining electrokinetic phenomena.

This paper presents a simple equation which appears to unify the Helmholtz-Smoluchowski and Schmid theories, defines with precision the distance between the plates of the equivalent condenser and, hopefully, provides a better basis for a physical understanding of the phenomenon of electroosmosis in porous media.

NOTATION

A = cross-sectional area of porous medium,

A_1 = concentration of wall charges expressed in ionic equivalents per unit volume of pore fluid (number of charges per volume),

a = cross-sectional area of capillary tube,

C = capacity of condenser,

C_s = shape factor,

d = parameter to characterize electric double layer,

E = applied electric field (potential gradient),

F = average electrical driving force per unit volume of electrolyte in capillary,

F_1 = 1 faraday (96,490 coulombs),

k = hydraulic permeability of porous medium,

k_e = electroosmotic permeability of porous medium,

L = length,

$\overline{L}$ = length of capillary tube,

M = mass,

m = number of capillaries per unit area of porous material,

m_n = number of capillaries per unit area of porous material with radius R_n,

n = porosity (also used for summation index),

Q = quantity of fluid discharged per unit time,

$\overline{Q}$ = electric charge,

q = flow volume per second through individual capillary,

R = effective radius of capillary,

R_n = effective radius of specific capillary,

r = radial coordinate in capillary,

dr = differential radial distance,

$\overline{r}$ = radial distance to circle of electrical gravitation,

T = time,

t = shear stress in fluid,

v_s = velocity of first moving layer (slip velocity),

V = average velocity of water migration in steady-state condition,

dv = differential change in velocity,

x_s = x coordinate of surface of immobile portion of electric double layer,

$x,\ y,\ z$ = rectangular coordinates,

ϵ = dielectric constant of fluid,

γ = fluid mass density,

π = 3.1416...,

π_n = pi product,

ρ = mobile excess electric charge density,

$\overline{\rho}$ = average mobile excess electric charge density,

σ = surface charge density,

τ = thickness of immobile portion of double layer,

μ = fluid viscosity,

ζ = zeta or electrokinetic potential, and

$d\theta$ = differential angle in polar coordinate system.

VARIABLES CHARACTERISTIC OF ELECTROOSMOTIC FLOW

It will be convenient to relate the variables characteristic of electroosmotic flow by use of dimensional analysis. The only restriction placed on this analysis is that a complete set of variables must be chosen which completely define a physical system. Within this limitation, variables may be chosen a priori. If only the balance between viscous and electric forces at steady-state conditions is considered and all complicating effects

discussed previously are ignored, the variables affecting electroosmotic flow can be simply delineated.

The shear stress, t, at any surface element in the capillary is proportional to the rate of change of velocity across the element dv/dr. The constant of proportionality is the coefficient of viscosity, μ, of the fluid. Thus,

$$t = \mu \frac{dv}{dr} \tag{1}$$

This equation implies that the shearing resistance to electroosmotic flow is related to a surface area of shear, a thickness of the shear zone, a velocity, and a coefficient of viscosity. If only electroosmotic flow in a uniform capillary tube is considered, it is reasonable to characterize the surface area by the variable R, the radius of the capillary; the shear zone by d, the characteristic distance of the mobile part of the double layer; the velocity by V, the average velocity of flow in a steady-state condition; and the viscosity by μ, the coefficient of viscosity of the fluid.

The electric driving force is a function of the electric field and the charge. Consequently, the variables E, the applied field (or potential gradient), and $\bar{\rho}$, the average excess mobile charge density, are introduced. (The characteristic volume has the same variable R introduced previously.) The point of application of both the electric and viscous forces is at the distance d from the surface of the immobile layer on the wall of the capillary. This is the same distance d introduced previously and it is discussed in considerable detail subsequently. At this point, however, d may most simply be considered a distance characterizing the electric double layer.

It is also convenient to introduce as a variable γ, defined as the mass density of the fluid in the capillary. This variable aids in the analysis and disappears from the final form of the expression developed.

Development of Relationship Among Variables

The variables necessary to characterize electroosmotic flow through a capillary tube under the influence of an applied electric field have been developed in the preceding section. They have the fundamental dimensions of mass (M), length (L), time (T), and charge (Q), as follows:

μ = coefficient of fluid viscosity, $M\ L^{-1}\ T^{-1}$;

γ = fluid mass density, $M\ L^{-3}$;
R = effective capillary radius, L;

V = average velocity of water migration in steady-state condition, $L\ T^{-1}$;
d = distance to characterize electric double layer, L;
$\bar{\rho}$ = average mobile charge density, $\bar{Q}\ L^{-3}$; and

E = applied electric field (or potential gradient), $M\ L\ T^{-2}\ \bar{Q}^{-1}$.

All other variables that might affect electroosmotic flow, such as temperature, time, surface conductance, nonuniform geometry of pores, heterogeneity of material, variable viscosity of pore fluid, electrolysis and possible ion exchange, are not considered further, and the system is assumed to be characterized completely by the seven variables. These assumptions are identical to those made in the development of the Helmholtz-Smoluchowski and Schmid equations. Consequently, the equations developed using them are subject to the same limitations as the Helmholtz-Smoluchowski and Schmid equations.

By applying the Buckingham pi theorem, a mathematical technique to reduce the number of variables of a system to a smaller number of dimensionless parameters that characterize it, three dimensionless parameters may be developed. They are obtained by considering the following three pi products:

$$\pi_1 = f_1 (E, V, R, \overline{\rho}, \gamma) \tag{2a}$$

$$\pi_2 = f_2 (d, V, R, \overline{\rho}, \gamma) \tag{2b}$$

$$\pi_3 = f_3 (\mu, V, R, \overline{\rho}, \gamma) \tag{2c}$$

Completing the analysis of these pi products, we arrive at the following dimensionless parameters:

$$\pi_1 = \frac{R \rho E}{V^2 \gamma} \tag{3a}$$

$$\pi_2 = \frac{d}{R} \tag{3b}$$

$$\pi_3 = \frac{VR\gamma}{\mu} \tag{3c}$$

However, $\overline{\rho} E$ (Eq. ... s equal to the average electrical driving force per unit volume of electrolyte in the capillary and can be denoted as F. Thus, if the variables selected for the analysis truly represent the behavior of the system, electroosmotic flow is completely defined as a function of three dimensionless parameters by the following equation:

$$f \left(\frac{RF}{V^2 \gamma}, \frac{d}{R}, \frac{VR\gamma}{\mu} \right) = 0 \tag{4}$$

The relationship among the variables in Eq. 4 must be valid for both the Helmholtz-Smoluchowski and Schmid conditions since no assumptions have, as yet, been made limiting the interval in which it is applicable. To develop the relationship among the dimensionless variables, several assumptions must now be introduced.

Lomize et al. ([4]) argued that the flow through capillaries in an electric field was laminar and similar to hydraulic flow through pipes. Consequently, they reasoned that the product of π_1 and π_3, which represent the friction factor and Reynolds number characteristic of hydraulic flow, must be equal to some dimensionless factor of proportionality that is a function of the physical and chemical properties of the system. They showed that this assumption was reasonable and productive but did not define the proportionality factor further.

If it is assumed that the proportionality factor is given by a function of π_2, the relationship among the dimensionless parameters may be written as:

$$\left(\frac{RF}{V^2 \gamma} \right) \left(\frac{VR\gamma}{\mu} \right) = f_4 \left(\frac{d}{R} \right) \tag{5}$$

or

$$V = \frac{R^2 F}{\mu} f_5 \left(\frac{d}{R} \right) \tag{6}$$

To proceed further, it is necessary to define the distance d and to relate it to the zeta potential. Since d is meant to characterize the mobile portion of the electric double layer from both the electrostatic and fluid mechanical point of view, it may be defined as the distance between the center of electrical gravitation of the mobile portion of the double layer and the surface of the immobile portion of the double layer. This definition is indicated for a segment of a capillary tube or for a flat plate in Figure 1a. (Detailed investigation of the final equation using existing double-layer theories has shown that the definition of d is valid.)

When the double layer is contained within a circular capillary tube, the locus of all points defining the center of electrical gravitation of the mobile portion of the double layer will lie on a circle, as shown in Figure 1b, which can be called the circle of electrical gravitation. It may be found by noting that the moment of mobile charges on one side is equal to the moment of charges on the other side. Thus,
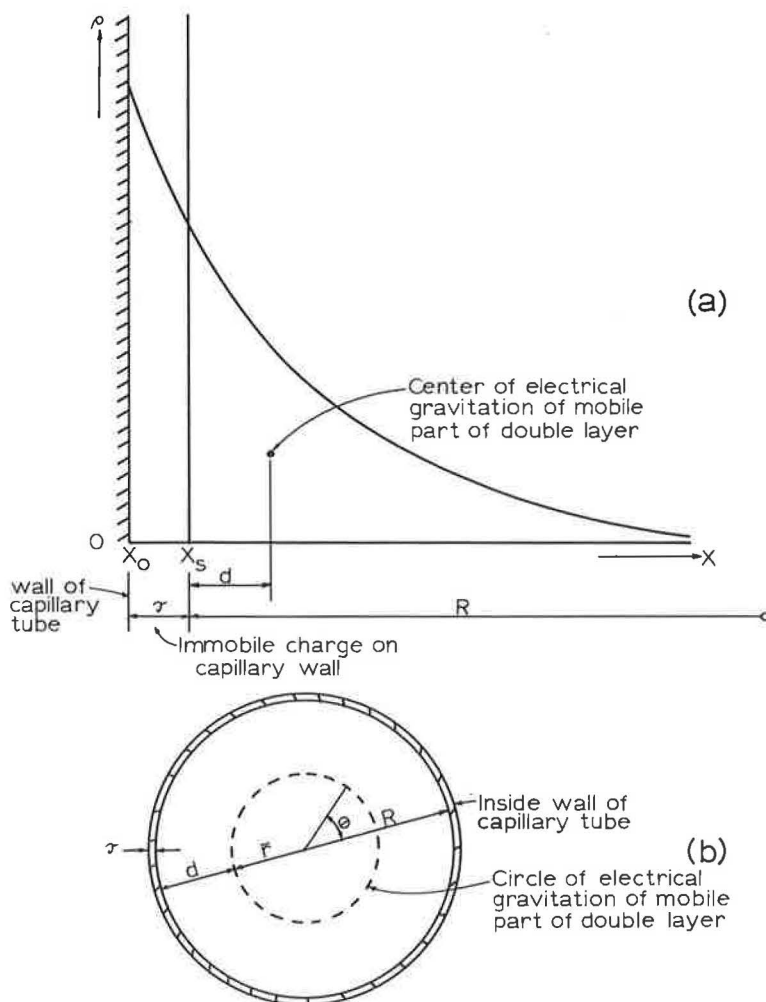
Figure 1. Definition of variables of electric double layer.

$$\iint_{\substack{\text{inside}\\\text{circle}}} \rho\,(\overline{r}-r) \cdot r \cdot dr \cdot d\theta = \iint_{\substack{\text{outside}\\\text{ring}}} \rho\,(r-\overline{r}) \cdot r \cdot dr \cdot d\theta \qquad (7a)$$

where $\overline{r}$ denotes the distance from the center of the capillary tube to the circle of electrical gravitation.

When the thickness of the double layer is small in comparison to the radius of the capillary and, as a result, there is effectively zero excess charge at the center of the capillary, Eq. 7a can be reduced to the simple form:

$$d = \frac{\displaystyle\int_{x_s}^{\infty} \rho \cdot x \cdot dx}{\displaystyle\int_{x_s}^{\infty} \rho \, dx} - x_s \qquad (7b)$$

For a circular capillary the distance d may be further defined (Fig. 1b) as:

$$d = R - \bar{r} \qquad (8)$$

Then by transforming the Helmholtz-Smoluchowski equation, a first approximation to the function $f_5 \left(\dfrac{d}{R}\right)$ may be obtained.

The Helmholtz-Smoluchowski equation, in the cgs electrostatic system, may be written as:

$$V = \frac{\zeta \epsilon E}{4 \pi \mu} \qquad (9)$$

where ζ denotes the zeta or electrokinetic potential, ϵ denotes the dielectric constant of the capillary fluid, and all other terms have been previously defined. The Helmholtz-Smoluchowski equation is, by virtue of the original assumptions made in its derivation, only valid for the large capillary and the thin double layer.

As a result of the presence of the electric double layer, a cylindrical condenser can be assumed to exist at the walls of the capillary. This is the assumption made by Helmholtz in his original derivation. The capacity, C, of the condenser is given by

$$C = \frac{\epsilon \bar{L}}{2 \log_e \dfrac{R}{\bar{r}}} \qquad (10)$$

where $\bar{L}$ is the length of the capillary tube and all other terms are as previously defined.

The zeta potential, ζ, is the electric potential across the equivalent condenser and must, therefore, charge, $\bar{Q}$, divided by the capacity of the condenser:

$$\zeta = \frac{\bar{Q}}{C} \qquad (11)$$

The ratio $R/\bar{r}$ can be transformed in the following manner:

$$\frac{R}{\bar{r}} = \frac{\bar{r} - \bar{r} + R}{\bar{r}} = 1 + \frac{R - \bar{r}}{\bar{r}} = 1 + \frac{d}{\bar{r}}$$

which, for the Helmholtz-Smoluchowski assumptions, is approximately equal to:

$$\frac{R}{\bar{r}} \neq 1 + \frac{d}{R} \qquad (12)$$

By substituting Eqs. 10 and 12 into Eq. 11 and noting that the average electric charge per unit volume $\bar{\rho}$ may be given as:

$$\bar{\rho} = \frac{\overline{Q}}{\pi R^2 \overline{L}}$$

it is found that

$$\zeta = \frac{2\pi\bar{\rho}R^2 \log_e\left(1 + \frac{d}{R}\right)}{\epsilon} \tag{13}$$

Eq. 13 shows a relationship between d and the zeta potential. By now substituting Eq. 13 into Eq. 9 we find that:

$$V = \frac{1}{2} \log_e\left(1 + \frac{d}{R}\right) \frac{R^2 F}{\mu} \tag{14}$$

in which F is, as stated previously, $\bar{\rho}E$ or average electrical driving force per unit volume of electrolyte in the capillary. It is also important to note that R refers to the effective radius of the capillary, which is defined as the radius through which flow takes place.

Eq. 14 is in the form of Eq. 6 where:

$$f_5\left(\frac{d}{R}\right) = \frac{1}{2} \log_e\left(1 + \frac{d}{R}\right) \tag{15}$$

Consequently, an equation has been developed for circular capillaries which contains:

1. All the variables required to satisfy the results of the dimensional analysis (Eq. 4),
2. These same variables in a relationship compatible with the assumptions that have been made, and
3. A first approximation of the missing function $f_5\left(\frac{d}{R}\right)$.

Since Eq. 14 has been developed from a transformation of the Helmhotz-Smoluchowski equation, it apparently satisfies the requirements of that theory. It now remains to show that Eq. 14 satisfies the requirements of the Schmid theory.

Development of Schmid-Poiseuille Equation

The Schmid theory was developed for microporous systems in which the charge in the pore fluid can be considered uniformly distributed. Schmid considered his theory valid for capillaries with radii of less than about 500 Å. By following the method of derivation of the Schmid-Poiseuille equation outlined by Winterkorn (10, 11), and introducing into the Poiseuille equation for flow through a capillary tube having a parabolic velocity distribution (no slip at walls) the electric force per unit volume P where

$$P = A_1 F_1 E \tag{16}$$

the following equation results:

$$q = \frac{\pi R^4 A_1 F_1 E}{8\mu} \tag{17}$$

where

q = the flow volume per second,
A_1 = concentration of wall charges expressed in ionic equivalents per unit volume of pore fluid (number of charges per volume),

E = electric potential gradient, and
F_1 = 1 faraday (96,490 coulombs).

However, the average velocity, V, of the water flowing through the capillary is equal to q/a where a is the area of the capillary cross-section. Thus, the average velocity is equal to:

$$V = \frac{1}{8} \frac{A_1 F_1 E R^2}{\mu} \tag{18}$$

Since the force function, $P = A_1 F_1 E$, is the electric force per unit volume of electrolyte in the capillary and has been designated previously as F, Eq. 18 can be rewritten as:

$$V = \frac{1}{8} \frac{R^2 F}{\mu} \tag{19a}$$

Once again the dimension R, appearing in Eq. 19a, refers to the effective radius of the capillary through which fluid flows. No fluid can flow through the zone occupied by the immobile layer on the capillary wall. Since by definition the dimension R is entirely within the mobile portion of the electric double layer (Fig. 1a), movement of fluid must be expected over the entire effective width of the capillary. As a consequence, slip must occur at the distance R from the center of the capillary tube and Eq. 19a, which has been derived assuming no slip conditions, should predict an average velocity that is too small.

If the general form of the Poiseuille equation is solved using the Schmid force function (Eq. 16), and assuming that slip occurs and the velocity of the first moving layer is given by v_S, the average velocity, V, is

$$V = v_S + \frac{1}{8} \frac{R^2 F}{\mu} \tag{19b}$$

It can be concluded, therefore, that the use of Eq. 19a is likely to predict a minimum average velocity of electroosmotic flow for microporous systems.

Eqs. 14 and 19a can be shown to be essentially the same, and a first indication is obtained that Eq. 14 may be a general form of the equation for electroosmotic flow if the factor $\frac{1}{2} \log_e \left(1 + \frac{d}{R}\right)$ is nearly equal to 1/8 when the Schmid conditions are imposed on the analysis. For these conditions in a circular capillary, the charge density ρ is a constant and the moment of charge on one side of the circle of electrical gravitation (Fig. 1b) must be equal to the moment of charge on the other side. Therefore, from Eq. 7:

$$\int_0^{\bar{r}} (\bar{r} - r) \cdot r \cdot dr = \int_{\bar{r}}^{R} (r - \bar{r}) \cdot r \cdot dr \tag{20}$$

Integrating Eq. 20 and rearranging terms leads to the following:

$$\frac{d}{R} = \frac{1}{3} \tag{21}$$

Substituting $d/R = 1/3$ into Eq. 15 produces a factor $\frac{1}{2} \log_e \left(1 + \frac{d}{R}\right)$ equal to 0.144.

This value exceeds 1/8 by about 15 percent, which is considered a reasonable check of Eq. 19a. Part of the difference results from the fact that Eq. 15 represents only a

first approximation to the missing function $f_5\left(\dfrac{d}{R}\right)$. Additional difference results from the assumption, for both the Helmholtz-Smoluchowski and Schmid conditions, that the slip velocity is zero. Recent work has shown that any slip velocity other than zero will have a relatively more important effect on the average velocity when small, rather than large, capillaries are considered.

It appears from the preceding discussion that a simple expression has been developed for circular capillaries which unifies, within reasonable limits, the Helmholtz-Smoluchowski and Schmid equations. This expression has the advantage of treating a range of capillary diameters and can be used together with existing double-layer theories to predict velocities under a wide range of conditions. Recent work has shown that Eq. 14 is entirely compatible with the double-layer theories presented by Bolt (1). Eq. 14 also leads to some interesting conclusions with regard to electroosmotic flow through porous media.

Implications for Porous Media

The average velocity of flow of water in a single capillary subjected to an electric field may now be approximated by Eq. 14. The total quantity of flow per unit time, q, through this capillary is given by:

$$q = \frac{\pi R^4 \bar{\rho} E}{2\mu} \log_e \left(1 + \frac{d}{R}\right) \tag{22}$$

where $\bar{\rho}E$ has been substituted for F.

It is apparent that the flow through the capillary is dependent on the capillary radius and that the flow through a group of capillaries of different radii cannot be truly a function of parameters like the average capillary radius or the porosity of the system. However, the error introduced by using these parameters can be shown to be small.

Expanding the logarithmic function in Eq. 14 in the Taylor series and using only the first term, d/R, to represent the entire series introduces into the equation an error that must be smaller than 17 percent. Consequently, the average velocity of flow, overstated by no more than 17 percent, may be represented as:

$$V = \frac{1}{2} \frac{dR \, \bar{\rho} E}{\mu} \tag{23}$$

Moreover, the average mobile charge density $\bar{\rho}$ is related to a uniform surface charge density by:

$$\bar{\rho} \pi R^2 = (-\sigma) \, 2\pi R \tag{24}$$

or

$$\rho = \frac{2(-\sigma)}{R} \tag{25}$$

where the minus sign indicates a surface charge opposite in sign to that in the mobile portion of the double layer.

By substituting Eq. 25 into Eq. 23, we find that

$$V = \frac{d(-\sigma) E}{\mu} \tag{26}$$

indicating that the average velocity of flow is, for the case of a uniform surface charge density, sensibly independent of radius of the capillary.

The outflow per unit time, q, for the individual capillary is a function of the area of the capillary cross-section:

$$q = a \cdot V \tag{27}$$

where a has previously been defined as the effective area of an individual capillary and is equal to πR^2. Therefore, for a bundle of m_n capillaries per unit area of radius R_n, discharging from a gross area A, the total discharge, Q, may be written as:

$$Q = \sum_0^n m_n \pi R_n^2 A \cdot V \tag{28}$$

However, the term $\sum_0^n m_n \pi R_n^2$ is exactly equal to the porosity, n, of the system. Thus,

$$Q = nA \cdot V \tag{29}$$

Eq. 26 is only correct to within 17 percent when a uniform charge density exists on the walls of the capillaries, the capillaries are straight, and the electric field is uniform. In a porous medium, such as soil, the charge density cannot usually be assumed to be uniform because of irregularities in the structure of some of the clay minerals and the common occurrence of several clay minerals intermixed with sand and silt grains. Thus, the velocity is most probably a linear function of capillary radius as indicated by Eq. 23. The capillary radius, in turn, may be related to the hydraulic permeability and porosity (3) by:

$$R = \left(C_s \frac{\mu}{\gamma} \frac{k}{n} \right)^{1/2} \tag{30}$$

where C_s denotes a shape factor that takes into account the tortuosity of flow channels in porous media. Substituting Eq. 30 into Eqs. 29 and 23 we find that:

$$Q = C_1 \left(\frac{kn}{\mu\gamma} \right)^{1/2} d \cdot \overline{\rho} \cdot EA \tag{31}$$

where C_1 is a constant related to the shape factor. Defining electroosmotic flow in a form analogous to Darcy flow as follows:

$$Q = k_e \cdot E \cdot A \tag{32}$$

where k_e represents an electroosmotic coefficient of permeability and E is the potential gradient, we find that

$$k_e = C_1 \left(\frac{kn}{\mu\gamma} \right)^{1/2} d \cdot \overline{\rho} \tag{33}$$

and k_e is related to the hydraulic permeability and the porosity of the system.

One side advantage of relating electroosmotic flow to hydraulic permeability as done here is that, in the form of Eq. 31, the electroosmotic flow equation includes a correction for the tortuosity of the flow path in the porous media. This correction factor is not exactly correct since C_1 is related to $\left(C_s \right)^{1/2}$, and the shape factor for electroosmotic flow may be different from that for hydraulic flow, but it is a convenient step in the proper direction.

Other implications of Eq. 14 are that electroosmotic flow is directly related to double layer thickness which is, in turn, related to pore ion concentration. Thus, electric conductivity measurements should be obtained when attempting to predict the usefulness (and economy) of electrokinetic treatment.

When applied to saturated soils, Eq. 14 implies that the higher the water content of the soil mass, the greater is the electroosmotic flow, except when the soil-water system becomes fluid and the soil particles are able to move. By definition, the fluid state would be expected at water contents in the neighborhood of the liquid limit of the soil. A reduction of the electroosmotic flow has been shown by Piaskowski (6) and Winterkorn (10) to occur at these water contents.

The relationship between surface charge density and velocity of flow leads to the conclusion that the effectiveness of electrokinetic treatment of soils should be related to the plasticity properties of soils since the higher the surface charge density, the higher are the expected Atterberg limits. Consequently, greater effectiveness of electroosmotic treatment would be expected in montmorillonitic soils than in kaolinitic soils.

CONCLUSIONS

A general equation for electroosmotic flow in circular capillaries appears to have been developed. The new equation has been checked against the Helmholtz-Smoluchowski and Schmid-Poiseuille equations, which are the two limiting cases. Its advantages are that it has a simple form, it can be used with any existing or improved double-layer theories, it permits the prediction of velocities for a wide range of capillary diameters, and it provides better physical insight into the process of electroosmotic flow than most existing theories. It is, however, subject to essentially the same limitations as most equations. Analysis of the new equation suggests that for a porous medium such as soil, the electroosmotic velocity of water flow is related to permeability, porosity, pore ion conductivity and soil plasticity properties. These variables must be investigated in determining the suitability of a soil for electrokinetic treatment.

ACKNOWLEDGMENTS

REFERENCES

1. Bolt, G. H. The Significance of the Measurement of the Zeta Potential and the Membrane Potential in Soil and Clay Suspensions. M. S. thesis, Cornell Univ., 1952.
2. Helmholtz, H. von. Ann. Physik Wiedemann. Vol. 7, p. 337, 1879.
3. Leonards, G. A. Foundation Engineering. New York, McGraw-Hill, 1962.
4. Lomize, G. M., Netushil, A. V., and Rzhanitzin, B. A. Electroosmotic Processes in Clayey Soils and Dewatering During Excavations. Proc. 4th Int. Conf. on Soil Mech. and Found. Eng., Vol. 1, pp. 62-67, 1957.
5. Oel, H. J. Zur Theorie der Electrokinetischen Ersheinungen. Z. fur Phys. Chem., Neue Folge, Vol. 5, pp. 32-51, 1955.
6. Piaskowski, A. Investigation on Electro-osmotic Flow in Soils in Relation to Different Characteristics. Proc. 4th Int. Conf. on Soil Mech. and Found. Eng., Vol. 1, pp. 89-92, 1957.
7. Schmid, G. Series of papers in Z. Electrochem., Vol. 54, p. 424, 1950; Vol. 55, pp. 229, 684, 1951; Vol. 56, pp. 35, 181, 1952.
8. Smoluchowski, M. von. Handbuch der Electrizitat und des Magnetismus. Vol. 2, p. 366. Leipzig, J. A. Barth, 1921.
9. Van Olphen, H. An Introduction to Clay Colloid Chemistry. N. Y., Interscience, 1963.
10. Winterkorn, H. F. Surface Chemical Properties of Clay Minerals and Soils from Theoretical and Experimental Developments in Electroosmosis. ASTM Sp. Tech. Pub. 142, pp. 44-52, 1952.
11. Winterkorn, H. F. Potentials in Moisture Migration. Bull. No. 1, Div. of Bldg. Res., N. R. C., pp. 86-101, 1955.

Discussion

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This paper is of considerable interest in that it provides a fresh approach to the problem of establishing the physical significance of the coefficent of electroosmotic permeability. The dimensional analysis used to derive the equation presented here closely parallels that used by Leonards (3) to establish the generalized Hagen-Poiseuille equation for hydraulic flow:

$$V = C_S \left(\frac{\gamma S}{\mu} \right) R_H^2 \tag{34}$$

where

V = superficial hydraulic flow velocity;
C_S = shape factor, introduced to account for the shape of the pore cross-section;
R_H = hydraulic radius;
γ = unit weight of fluid;
S = hydraulic gradient; and
μ = coefficient of absolute viscosity of the fluid.

Thus, it is not surprising that a similar result can be obtained from a modification of Eq. 34. The required modification is achieved by replacing the hydraulic gradient, S, by an equivalent electroosmotic gradient, S_e, which may be written as:

$$S_e = f \left\{ \frac{E \bar{\rho}}{\gamma} \right\} \tag{35}$$

where

E = applied electric field, and
$\bar{\rho}$ = average excess charge density of mobile portion of diffuse ion layer.

By the use of this substitution, it is possible to write an electroosmotic flow equation of the form

$$V = C_{S_e} \frac{\gamma}{\mu} R^2 \cdot f \left\{ \frac{E \bar{\rho}}{\gamma} \right\} \tag{36}$$

where

V = superficial electroosmotic flow velocity,
C_{S_e} = electroosmotic shape factor, and
R = electroosmotic radius, related to the hydraulic radius.

The approximations used in the original presentation allow the evaluation of the electroosmotic gradient, S_e, as

$$S_e = f \left\{ \frac{E \bar{\rho}}{\gamma} \right\} \cong \frac{d}{R} \cdot \frac{E \bar{\rho}}{\gamma} \tag{37}$$

where d is a parameter introduced to characterize the properties of the diffusion layer (see Fig. 1a). Thus, Eq. 36 becomes:

$$V = C_{S_e} \frac{R}{\mu} d \bar{\rho} E \tag{38}$$

and if

$$Q = n A V \tag{39}$$

where

Q = discharge per unit time,
n = equivalent porosity (based on free volume of pores), and
A = cross-sectional area of soil,

Eq. 39 becomes

$$Q = C_{S_e} \frac{R}{\mu} d \bar{\rho} n EA \tag{40}$$

If it is further assumed that $R \simeq R_H$, a combination of the Hagen-Poiseuille equation with Darcy law yields the relationship:

$$Q = \frac{C_{S_e}}{\sqrt{C_s}} \left\{ \frac{kn}{\mu\gamma} \right\}^{1/2} d \bar{\rho} EA \tag{41}$$

where k is hydraulic permeability.

Electroosmotic flow has been described (13) by the empirical equation:

$$Q = k_e EA \tag{42}$$

where K_e is electroosmotic permeability. Using this relationship,

$$\text{Constant } C_1 = \frac{C_{S_e}}{\sqrt{C_s}} \tag{43}$$

Therefore, Eq. 41 may be simplified to

$$k_e = C_1 \left\{ \frac{kn}{\mu\gamma} \right\}^{1/2} d\bar{\rho} \tag{44}$$

which is Eq. 33 of the paper under discussion.

It would seem, however, that C_1 is related to $(C_s)^{-1/2}$ and, thus, serves to generalize by taking into account, at least partially, any deviation from the circular in the shape of the cross-section of the soil pores. It does not, however, offer any correction for the tortuosity of the flow path within the soil.

From Eqs. 41 and 44 and from Eq. 14 of the paper under discussion, it would seem that the effectiveness of electroosmotic treatment would vary directly with the excess charge of the cations in the mobile portion of the double layer. The high surface charge density and, perhaps more important, the high specific surface associated with montmorillonitic clays would reduce this quantity to below that of a less active kaolinitic soil, all other factors being equal. The reduction in the excess charge of the diffuse ion layer would be at least partially offset by an increase in the parameter d and in the hydraulic permeability, but experimental evidence shows that electroosmotic permeability decreases slightly with increasing activity. Casagrande (13) found that k_e — 2×10^{-5} cm/sec for Na bentonite at a water content of 170 percent and 5×10^{-5} cm/sec for a less active clayey silt.

The efficiency of electroosmotic dewatering, as opposed to hydraulic dewatering, may be characterized by the ratio k_e/k. In the case of the two soils mentioned, k_e/k is 2×10^6 for the Na bentonite and 6.25×10^2 for the clayey silt. Thus, even though the electroosmotic permeability of the bentonite was found to be slightly less than that of the clayey silt, its suitability to electroosmotic treatment is considerably greater.

It should also be pointed out that a significant change in outflow under a constant macroscopic electric potential gradient can occur over a period of time, particularly in active soils at high water contents. It would appear that this effect is due largely to

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local changes in the resistivity of the soil-water system which lead to changes in the microscopic electric gradient (12).

References

12. Cambefort, H., and Caron, C. Electro-osmose et Consolidation Electro-Chemique des Agriles. Géotechnique, Vol. 11, pp. 203, 1961.
13. Casagrande, L. Electro-osmosis in Soils. Géotechnique, Vol. 1, No. 3, 1949.

M. I. ESRIG and S. MAJTENYI, Closure—Mr. Leitch's discussion raises several important questions about electroosmotic flow of water in soils and about the equations we have developed. These questions are related to the use of the Poiseuille equation in characterizing electroosmotic flow, the effect of the shape and tortuosity of the soil pores on this flow, the physical significance of the new equation we have proposed, and the effects of time on electroosmotic flow.

As Mr. Leitch has suggested, the use of the Poiseuille equation, whether or not it is developed from a dimensional analysis, to characterize electroosmotic flow in capillaries can, under a limited set of circumstances, be correct. Use of this equation is only correct when the driving force is uniform across the cross-section of the capillary. This limitation was recognized by Winterkorn ($\underline{10}$, $\underline{11}$) when he developed what we have termed the Schmid-Poiseuille equation that characterizes electroosmotic flow in microcapillaries. However, when the capillary diameter becomes so large that the Helmholtz theory is applicable (d/R is small and approaches a minimum value), the electrical driving force is no longer uniformly distributed but is localized in a small region near the capillary wall. For this condition, the Poiseuille equation is not applicable.

Mr. Leitch's implication, that the introduction of the electroosmotic force function into the Poiseuille equation produces simply and quickly the new equation for electroosmotic flow, obscures the main problem (and contribution) of the paper. That is, a first approximation to the function f_s d/R has been developed which unifies the Helmholtz-Smoluchowski and Schmid theories. Using Mr. Leitch's approach, which is an extrapolation of the Poiseuille equation, it is not possible to develop this function.

Mr. Leitch's comments about the correction for shape and tortuosity are correct if the factor C_s is defined in accordance with the development presented by Leonards ($\underline{3}$) only as a correction factor to account for the shape of the capillary cross-section. However, it was our intention to define this factor as a combined shape and tortuosity correction, since these corrections are essentially inseparable when determining soil permeabilities. In our opinion, such a definition does not change the analysis presented in the paper. In addition, if it is assumed that the imposition of the electrical field on the soil mass does not alter the shape or tortuosity of the capillaries (an assumption that may be subject to some question) it is apparent from Eq. 41 that $C_1 = C_s^{1/2}$. Since C_s must be less than unity, it is also readily seen that C_1 is closely equal to unity for a wide range of values of C_s. Thus, in the form of Eq. 31, the coefficient C_1 can probably be assumed equal to unity with a loss in accuracy which is small in comparison to the many other uncertainties present when one tries to predict electroosmotic flows.

Mr. Leitch has also pointed out the rather important interrelation of the parameters d and $\bar{\rho}$. He has argued that the product of d and $\bar{\rho}$ should increase with soil activity and that the electroosmotic permeability of the soil should, therefore, increase. He points out, however, that increasing the activity of a soil from that of a clayey silt to a bentonite has been shown to decrease k_e. We are in agreement with Mr. Leitch's analysis and have experimental evidence to suggest that it is correct but that he has not carried it quite far enough. For example, referring to Eq. 31, which is only a simplification of Eq. 14 into which the relevant engineering index properties of soil have been introduced, it is apparent that the net effect of a reduction in the permeability of soil from that of the clayey silt (8×10^{-8} cm/sec) to that of the bentonite (1×10^{-11}

cm/sec) would be a decrease in k_e. A further decrease could be expected because the pore fluid conductivity of the sodium bentonite was reported to be 5 times greater than that of the clayey silt, tending to decrease the parameter d significantly. Complicating this sort of qualitative analysis is the fact that in bentonite a reduction in electroosmotic outflow would be expected as a result of the presence of positive charges on the edges of the particles while negative charges are present on the faces. Consideration of these factors, together with those indicated by Mr. Leitch, leads to the conclusion that qualitative evaluation of our equation predicts changes in k_e in agreement with experimental evidence.

Finally, we have specifically excluded from our analysis the effects of time on the electroosmotic permeability of soils. It is recognized that physical and chemical changes occur with time in soils subjected to an electric field. These changes will change the electroosmotic permeability of the soil, generally tending to decrease it. We only intend that our analysis be considered applicable for a very short period after an electric field is applied.