GEOMETRY EFFECTS FOR SPECIFIC ELECTRICAL CONDUCTANCE IN CLAYS AND SOILS

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ABSTRACT

A SYSTEMATIC study of the influence of salinity and clay content on the electrical conductivity of sodium-illite clay gels shows that the geometry or "formation resistivity factors" of such systems can adequately be described by the model of oblate ellipsoids, used to simulate the shape of the clay particles. This conclusion is in agreement with the results previously obtained on kaolinite and montmorillonite clays. An axial ratio of 16 was found for the illite clay particles.

On the basis of Burger's and Maxwell's equations for electric flow through porous media, formulae are derived for calculating the electrical conductivity of mixed systems, *i.e.* "clay 1 + clay 2 + electrolyte solution" and "clay + spherical particles + electrolyte solution". The electrical conductivity of these systems is expressed in terms of the shape parameters, surface conductances, specific surfaces and volume concentrations of the constituents. The type of equation can eventually lead to an explanation (in terms of a non-uniform particle shape distribution) of the anomalous geometry effects in some clays.

Experimental results conform fairly well to the equations. Glass powder at volume fraction between 0.18 and 0.60 added to a 17.4% montmorillonite gel acts as an inert diluent on the specific electrical conductivity of the mixture. For a mixture of 1 part montmorillonite to 9 parts kaolinite, the measured specific electrical conductivity agrees within about 10% with the predicted over the range studied (volume fraction of montmorillonite: 0.035 to 0.039; mixture porosity: 0.61 to 0.650; salt concentration range: 0.5 N to 2 N NaCl).

INTRODUCTION

A QUANTITATIVE understanding of the relative importance of the factors affecting the movement of an ion through a clay–water system is a fairly complex task. It is a well-known fact that an ion, when moving through a colloidal medium such as a clay plug, is drastically reduced in its mobility. Several explanations have been offered to account for this phenomenon. The first one, commonly called the tortuosity effect, is the result of the reduction in cross sectional area available for ion movement and the increased path length to which any moving species is subjected. This problem has experimentally been approached for soils by gaseous diffusion (Penman, 1940*a*, 1940*b*; Leonard and Low, 1964) and for clays by diffusion of uncharged

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molecules (Bloksma, 1957). The electrical interaction, which includes coulombic as well as polarization and dispersion effects, is also considered to be a very important factor. A quantitative understanding of this effect has been attempted along the lines of the transition theory of rate processes (Glasstone, Laidler, and Eyring, 1941, p. 524) by Lai and Mortland (1961, 1962). A third effect which has been proposed by Low (1962) could be found in the particular properties, more specifically in a different structural arrangement of the water in the immediate vicinity of the clay surfaces. Differences in partial specific volume of the surface water (Anderson and Low, 1958), activation energy data for ion movement and self-diffusion data for deuterium oxide in clays (Dutt and Low, 1961) support this viewpoint. Since the observed mobility of an ion in such systems is a complex result of these three, and possibly more, effects, it is important to attempt a separation of the parameters involved in order to obtain a clearer view as to which of these factors is the predominant one. This can eventually lead to a better understanding of some of the problems in plant nutrition and electric log interpretation.

The fact that tortuosity effects should not be relevant to the values of the activation energy for ion movement has been used by Low (1958) in an effort to exclude one of the parameters involved. A great part of our efforts has recently been directed towards a quantitative evaluation of the "formation resistivity factors" in various clays, using electrical conductivity measurements. From a study of the conductive properties of two kaolinite and two montmorillonite clays (Cremers and Laudelout, 1965*a*), it was concluded that the model of oblate ellipsoids can very well describe the shape of the clay particles and that each clay could definitely be characterized by a value of the axial ratio of its particles. The purpose of the present paper is firstly to examine if the same type of relationship holds for an illite clay, and secondly to derive equations which describe geometry effects in systems such as mixtures of clay and spherical particles as well as mixtures of two different clays.

THEORETICAL

The theoretical calculation of the electrical conductivity of heterogeneous systems has frequently been attempted and numerous equations have been proposed for various particle geometries (Maxwell, 1887; Burger, 1919; Fricke, 1924; Bruggeman, 1935; Böttcher, 1945). An excellent review on these problems has recently been published by Meredith and Tobias (1962). The diversity in the equations presented lies in the nature of the simplifying assumptions which are made in the theoretical approach to this very complex problem.

The basic assumption which underlies Maxwell's equation for the electrical conductivity of dispersions of spherical particles is that the electric field (or conductance) around a particle is identified with the electric field (or conductance) in the continuous phase. This amounts to neglecting any dis-

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turbing interactions from neighbouring particles. The application of this equation can therefore be expected to be valid for dilute dispersions only; nevertheless, in the case of non-conducting particles, experimental results agree fairly well with the theory up to volume concentrations as high as 60% (Clark, 1948; Meredith, 1959). Burger (1919) has presented an equation for the case of ellipsoidal particles; when the three axes of the ellipsoid are equal, his equation takes the form of Maxwell's and should therefore be considered as subject to the same limitations.

The proposed equations for the calculation of the electrical conductivity of "two component" heterogeneous systems are based on the following assumption: The system "solution + component I" is a continuous phase with a uniform electric field (the initial electric field in the homogeneous phase reduced to a certain extent by the presence of the non-conductive component I); a second component is then randomly distributed in this system to give the "two component" mixture.

Clay + Electrolyte Solution

It has been previously shown (Cremers and Laudelout, 1965*a*) that the specific electrical conductivity of a clay gel can be written as

$$K = \frac{K_1}{F} + \Delta\lambda \tag{1}$$

where F is the "formation factor" by which the solid matrix reduces the electrical conductivity K_1 of the intermicellar solution and $\Delta\lambda$ stands for the volume conductance contribution of the excess or surface conductance of the clay. The formation factor, introduced by Archie (1942), is thus defined as the ratio of the electrical conductivity of an electrolyte solution to that of a fictitious surficially inert porous medium filled with that solution and which has the same geometry as the actual porous medium of interest. $\Delta\lambda$ is then *operationally defined* as the difference between the conductivity of a gel and that of the electrolyte solution, the latter reduced by a factor appropriate to the tortuosity of the medium. This $\Delta\lambda$ term can therefore be meaningful only if F can be determined.

Apparently, this type of relationship has been proposed (1950) by Patnode and Wyllie for the conductivity of "dirty sands"; the second term in their equation represents the conductivity of the "conductive solids" as distributed in the core, a concept which was subsequently discussed by Wyllie and Southwick (1954). Here, the situation is entirely different. Equation (1) does not assume that the overall conductivity of the system is the sum of two conductivities in parallel; it does not even assume that the conductivity of the solution in the pores is identical to the conductivity of that solution without the clay. This approach is entirely analogous to the problem of defining surface adsorption in heterogeneous media. Adsorption or extent of surface are in their essence relative concepts and have to be defined with

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respect to something. Here our reference point is the solution conductance free from charged surfaces. The equation does not pretend to give a microscopic picture of the range of conductivities the solution may exhibit. It merely replaces a supposedly continuous distribution of conductivities by two values the first of which is our reference value for the solution and the second a space average of the excess conductance in a zone the extent of which is, geometrically speaking, undefined. Provided F is determinable, the operationally defined quantity $\Delta\lambda$ will tell us the extent of effect of a clay surface according to conditions of salinity, ion type and clay content.

Cremers and Laudelout (1965*b*) have already given evidence that one may use the same F factor for computing $\Delta\lambda$ from the specific surface conductance of the clay. The justification of such a procedure was essentially based on the isoconductivity phenomenon. When the same F factor is taken, then the surface region through which this excess conductance is averaged is conventially taken to be the same as the region through which an electrolyte solution would produce such a conductivity in a geometrically identical gel.

The $\Delta\lambda$ term is then to be expressed by

$$\Delta\lambda = \frac{\lambda_s S_c}{F\phi} = \frac{FK - K_1}{F} \tag{2}$$

where S_c/ϕ is the "cell factor" used by Street (1956*b*, 1963), *i.e.* the ratio of surface of solid per unit volume of gel S_c to the porosity ϕ. For a system of oblate ellipsoids (the assumed model for the shape of the clay particles) F is related to the porosity by Burger's equation* (1919)

$$F = 1 + k\frac{1 - \phi}{\phi} \tag{3}$$

where k is a parameter which depends on the axial ratio of the nonconducting solid particles. The electrical conductivity of a clay plug may accordingly be written as

$$K = \frac{K_1\phi}{\phi + k(1 - \phi)} + \frac{2.5\ \lambda_s S_w(1 - \phi)}{\phi + k(1 - \phi)} \tag{4}$$

where S_w is the specific surface of the clay. A value of 2.5 has been used for the density of the clay material. For a system of spherical particles with surface conductance, this equation takes the form of the one presented by Street (1956*a*). It should be emphasized that the linear relationship between K and K_1, as suggested by equations (1) and (4), can only be expected to be valid within a rather limited salinity range. Considerable difficulties arise at low salt concentrations as the result of changes in surface conductance. This discussion will essentially be limited to highly saline systems.

* This equation is formally identical with the one found by Fricke (1924):

$$F = \frac{x + 1 - \phi}{x\phi}.$$

The parameter x is related to k by: $k = 1 + 1/x$. x takes the value 2 for spheres.

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*Mixture of Two Solid Phases in an Electrolyte Solution**

The calculation of the electrical conductivity of a system composed of two different clays as the solid phases will be given. According to equation (4) the electrical conductivity of a clay plug (clay I + solution) can be re-written as

$$K = \frac{K_1(1 - \rho_1') + 2.5\,\lambda_{s1}S_{w1}\rho_1'}{1 + \rho_1'\,(k_1 - 1)} \tag{5}$$

where $\rho_1' = \dfrac{V_1}{V_1 + V_w}$, *i.e.* the volume fraction of clay I in the system "clay I + solution".

Introducing a volume V_2 of clay II in this system, the conductivity of the mixture would be

$$K_m = \frac{\{[K_1(1 - \rho_1') + 2.5\lambda_{s1}S_{w1}\rho_1']/[1 + \rho_1'(k_1 - 1)]\}(1 - \rho_2) + 2.5\lambda_{s2}S_{w2}\rho_2}{1 + \rho_2(k_2 - 1)} \tag{6}$$

where

$$\rho_2 = \frac{V_2}{V_1 + V_2 + V_w},$$

i.e. the volume fraction of clay II in the mixture.

Since

$$(1 - \rho_1')(1 - \rho_2) = \left(\frac{V_w}{V_1 + V_w}\right)\left(\frac{V_1 + V_w}{V_1 + V_2 + V_w}\right)$$

which is the porosity of the mixture ϕ,
and since

$$\rho_1'(1 - \rho_2) = \left(\frac{V_1}{V_1 + V_w}\right)\left(\frac{V_1 + V_w}{V_1 + V_2 + V_w}\right)$$

(which is the volume fraction of clay I in the mixture ρ_1), equation (6) takes the following form after rearrangement:

$$K_m = \frac{K_1\phi}{[1 + \rho_2(k_2 - 1)]\{1 + [\rho_1(k_1 - 1)/(1 - \rho_2)]\}} + \frac{2.5\lambda_{s1}S_{w1}\rho_1 + 2.5\lambda_{s2}S_{w2}\rho_2\{1 + [\rho_1(k_1 - 1)/(1 - \rho_2)]\}}{[1 + \rho_2(k_2 - 1)]\{1 + [\rho_1(k_1 - 1)/(1 - \rho_2)]\}} \tag{7}$$

where the two terms refer to K_1/F and $\Delta\lambda$ respectively.

* The following symbols will be used: K_m: Specific electrical conductivity of the system "Clay I + clay II + electrolyte solution". K_1: Specific electrical conductivity of the electrolyte solution. K: Specific electrical conductivity of the system "clay I + electrolyte solution". k_1: geometry parameter of clay I. k_2: geometry parameter of clay II. V_1: volume of clay I per cm³ of gel. V_2: volume of clay II per cm³ of gel. V_w: volume of solution per cm³ of gel. λ_{s_1}: surface conductance of clay I. λ_{s_2}: surface conductance of clay II. S_{w_1}: specific surface of clay I. S_{w_2}: specific surface of clay II.

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If only one solid phase is present, equation (7) reduces to equation (5). When the second solid phase is inert spherical particles then $\lambda_{s_2}S_{w_2}$ is negligible compared to $\lambda_{s_1}S_{w_1}$ of clay. Since $k_2 = 1.5$ for spherical particles, equation (7) takes the form

$$K_m = \frac{2K_1\phi}{[(2 + \rho_2)/(1 - \rho_2)][(1 - \rho_2) + \rho_1(k - 1)]} + \frac{5\rho_1\lambda_{s_1}S_{w_1}}{[(2 + \rho_2)/(1 - \rho_2)][(1 - \rho_2) + \rho_1(k - 1)]} \quad (8)$$

MATERIALS AND METHODS

The homo-ionic sodium clays used in this study, namely an illite (Versailles-France), a Boluvit kaolinite (Germany), and a Camp-Berteau montmorillonite (Morocco) were prepared by a saturation-separation procedure extensively described elsewhere (Martin and Laudelout, 1963; Cremers and Laudelout, 1965*a*). Some of the characteristics of these clays are summarized in Table 1. All measurements reported have been carried out at 25°C, using a Wayne–Kerr conductivity bridge (1592 c.p.s.) and a conductivity cell of the type described elsewhere (Cremers and Laudelout, 1965*a*). Dry weights which were obtained by overnight desiccation were corrected for salt content.

TABLE 1.—CATION EXCHANGE CAPACITY AND SPECIFIC SURFACE OF THE THREE CLAYS USED

Clay type	Cation exchange capacity (meq/100 gr)	Specific surface (m^2/gr)
Montmorrillonite of Camp-Berteau	100	750
Boluvit kaolinite	4.3	20
Illite	15.0	136

Dry weights were converted into volume fractions by using 2.5 and 3 (pycnometrically determined) for the densities of the clay materials and glass powder respectively. The mixed systems were prepared by carefully mixing two clay gels (obtained by the usual technique from suspensions which were equilibrated with solutions of identical concentration containing the two different clays, or by mixing a clay gel and purified glass powder.

RESULTS AND DISCUSSION

Sodium-Illite Clay Gels

Figure 1 represents the variation of the specific electrical conductivity of Na-illite clay gels, prepared by ultracentrifugation or pressure membrane techniques, as a function of clay content and for various salt concentrations (varying from 0 to 2.2 N NaCl). Each of the experimental points on each

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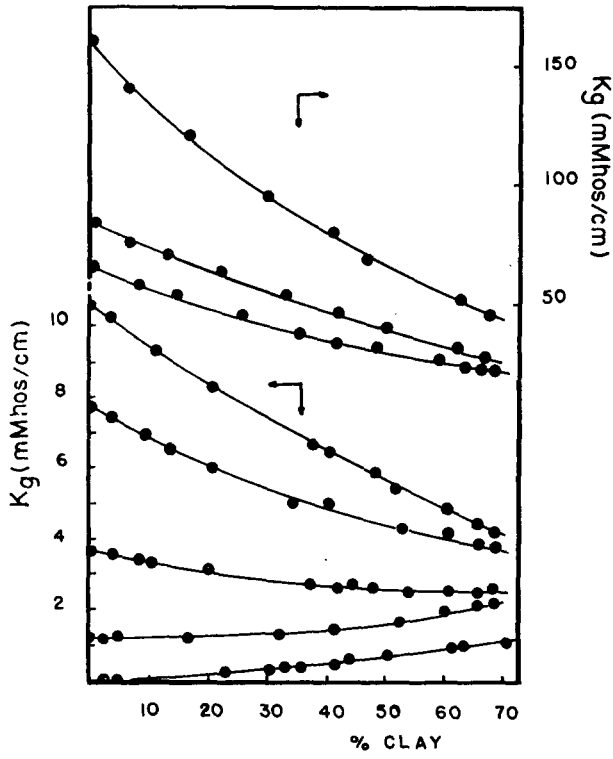


FIG. 1. Variation of the specific electrical conductivity (mmhos/cm) of sodium-illite claygels with their clay content (% by weight) as caused by expelling the NaCl solution in which the clay was originally suspended. The points on the ordinate represent the conductivities of the aqueous solutions. The upper part of the graph refers to a 0.7–2.2 N NaCl and the lower part to a 0–0.1 N NaCl concentration range.

curve refers to a clay gel prepared from a clay suspension for which the conductivity of the equilibrium solution is given by the point on the ordinate. Although some minor differences exist, the curves show the same general trend as those obtained for kaolinite (Cremers and Laudelout, 1965*a*). It is seen that the electrical conductivity steadily decreases if K_1, the conductivity of the equilibrium solution, is higher than about 2 to 3 mmhos/cm. In the case of lower K_1 values, the reverse is observed.

The formation factor of a clay plug of given clay content can be obtained graphically by applying equation (1). The results are shown in Fig. 2 where for a series of clay contents, varying from 10 to 60% by weight, the conductivities of the gels (as read from the curves in Fig. 1) have been plotted against the conductivities of the corresponding equilibrium solutions. It can be seen that for each particular clay content, a linear relationship exists

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between K_g and K_1. The reciprocal of the slope of each line yields the value of the formation factor for the corresponding clay content. All these lines show a common intersection point with the diagonal; This corresponds to the isoconductivity point as defined by Dakshinamurti (1960). The meaning of this intersection point has recently been discussed elsewhere (Cremers and Laudelout, 1965*b*). The scope of the present paper will be limited to considerations of geometry only.

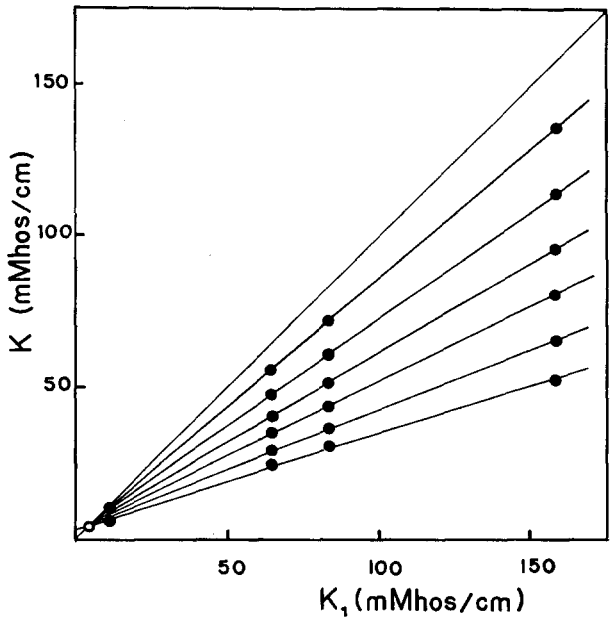


FIG. 2. Specific electrical conductivity (mmhos/cm) of sodium-illite clay gels K vs. specific electrical conductivity of the respective "equilibrium solutions" K_1, at different porosities varying from 0.96 (top) to 0.625 (bottom).

The procedure just described yields a set of $F - \phi$ pairs; if the model of oblate ellipsoids for the shape of the particles is valid, then the insertion of each pair into equation (3) should give identical values of k for all porosities studied. This is illustrated in Fig. 3 where the $1/F$ values, obtained from Fig. 2, have been plotted against the corresponding porosities. The average value of $k = 4.3$ has been used to calculate the curve according to equation (3). A series of k values for a number of axial ratios of oblate ellipsoids is given in Table 2. By using a graph "k versus axial ratio", a value of 16 was obtained for the illite particles. Figure 3 clearly demonstrates that equation (3) describes fairly accurately the relationship between the formation factor and the porosity of these clay gels.

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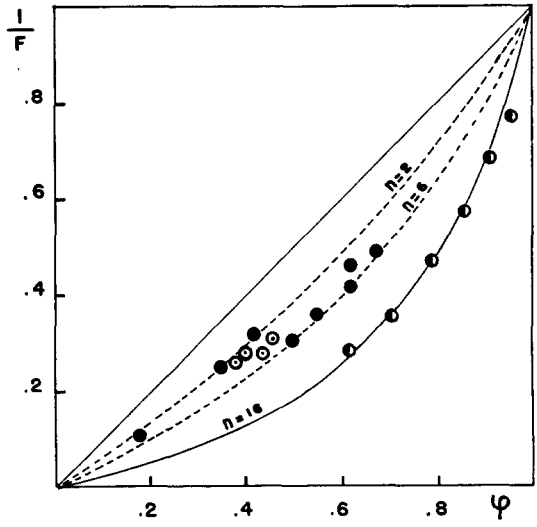


FIG. 3. Reciprocal of the formation factor of soil and clay plugs vs. the porosity. ◐ : Illite clay. ⊙ : Illitic soil. ● : Results of Penman obtained by gaseous diffusion in soils.

TABLE 2.—GEOMETRY PARAMETERS k FOR OBLATE ELLIPSOIDS CALCULATED FOR VARIOUS AXIAL RATIOS

Axial ratio	k
1	1.50
4	1.91
10	3.10
20	5.19
30	7.33
40	9.44
60	13.90

TWO COMPONENT SYSTEMS

The usefulness of equation (8) has been checked by measuring the electrical conductivity of gels containing various proportions of Na-Camp Berteau montmorillonite and glass powder. A clay gel containing 17.4% clay has been prepared from a suspension in which the equilibrium solution conductance was 99 mmhos/cm. Five mixtures were then prepared by thoroughly mixing various amounts of glass powder with the 17.4% gel. The results are shown in Fig. 4 where the conductivities of the mixtures have been plotted against the volume fraction of the glass powder present. The "theoretical" curve has been

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calculated according to equation (8) using values $k=8.6$ and $\lambda_s=4\times10^{-9}$ mhos, obtained from our previous investigations. It is evident that equation (8) is very useful in describing the experimental results.

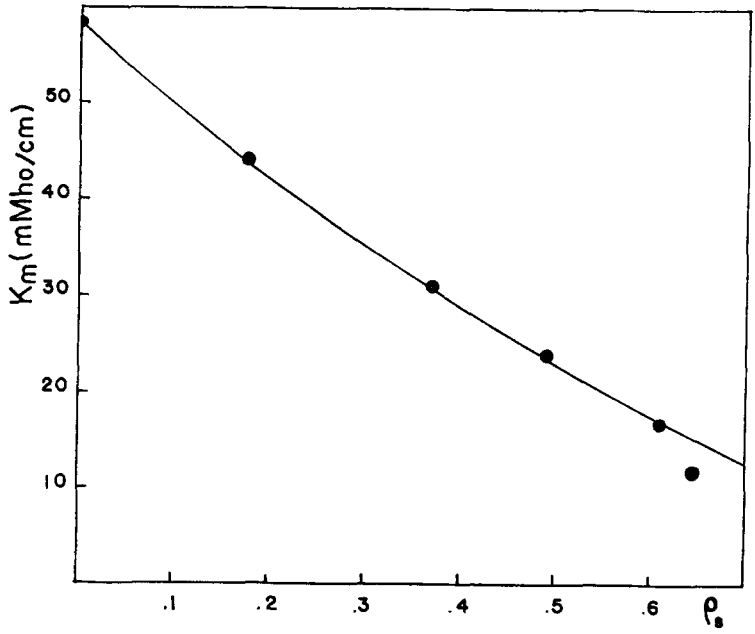


FIG. 4. Electrical conductivity of a mixture of Na-montmorillonite clay and glass powder vs. the volume fraction of the glass powder. The theoretical curve has been calculated according to equation (8). Clay content of the initial gel is 17.4% by weight. $k_{\text{montm.}} = 8.6$, $\lambda_s = 4 \times 10^{-9}$ mhos.

In order to verify equation (7), two gels at three electrolyte levels and containing different amounts of Na-Boluvit and Na-Camp Berteau montmorillonite were prepared. The weight proportion was kept constant in all preparations, namely montmorillonite/kaolinite $= \frac{1}{9}$. The results are summarized in Table 3. The k and λ_s values used in the calculations are those obtained from measurements in pure clay systems. In view of the considerable complexity of such mixtures, the agreement between the experimental and calculated conductivities may be deemed fairly satisfactory.

It is quite interesting to examine to what extent the geometry factor would vary in a system composed of an electrolyte solution in which oblate ellipsoids of two different shapes have been dispersed. Figure 5 shows the variation of the reciprocal of the formation factor as a function of porosity (according to the first term of equation 7) for such a system. The solid curves correspond to a one-solid phase system and the dotted curve refers to a

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TABLE 3.—COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE ELECTRICAL CONDUCTIVITY OF CLAY MIXTURES. THE WEIGHT PROPORTION MONTM./KAOL. IS KEPT CONSTANT IN ALL SAMPLES: 1/9. THE FOLLOWING VALUES FOR k AND λ_s (OBTAINED IN PREVIOUS WORK) WERE USED IN THE CALCULATIONS Na-CAMP-BERTEAU MONTMORRILONITE: $k = 8.6$, $\lambda_s = 4.10^{-9}$ MHOS; Na-BOLUVIT KAOLINITE: $k = 3.40$, $\lambda_s = 1.10^{-8}$ MHOS

				(mmhos/cm)	
K_1	ϕ	$\rho_{kaol.}$	$\rho_{montm.}$	$K_{mexp.}$	$K_{mcalc.}$
45.0	0.610	0.350	0.039	16.7	13.0
	0.613	0.349	0.038	16.4	13.0
79.4	0.623	0.340	0.037	21.0	18.6
	0.616	0.350	0.038	17.5	17.2
140.0	0.648	0.317	0.035	31.3	29.8
	0.634	0.330	0.036	29.0	28.7

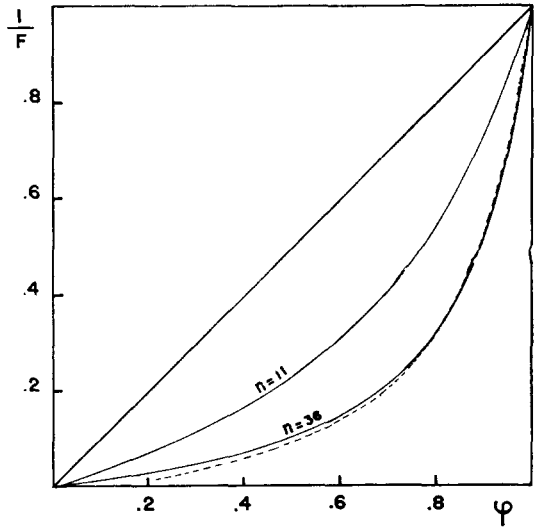


FIG. 5. Reciprocal of the formation factor vs. the porosity for heterogeneous systems composed of oblate ellipsoids; the solid curves refer to axial ratios of 11 and 36 respectively. The dotted curve, calculated from the first term of equation (7), corresponds to a mixture of both in a 1/9 proportion.

two-solid phase system. It can be seen that below porosities of about 70% the tortuosity effect becomes higher in the mixture than in the case of the one-solid phase system which has the flattest particles. This type of curve has previously been observed (Cremers and Laudelout, 1965*a*) in the case of a

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calcium–montmorillonite clay. It may be that the deviation of the geometrical behaviour from the "theoretical curve" in this case could be connected with a non-uniform particle shape distribution.

GEOMETRY EFFECTS IN SOILS

It can be seen that the proposed equations could serve as a basis for predicting geometry effects in natural soils, provided clay content and clay type are known. To test this, an illitic soil which contained about 10% clay was washed several times with a NaCl solution of about 1.6 N ($K_1 = 130$ mmhos/cm). Four plugs were then prepared using an ultracentrifuge and the conductivities measured. Porosities were calculated from dry weights. For such systems with low clay content and high salinity, we can write

$$\frac{K_g}{K_1} = \frac{1}{F_a} \simeq \frac{1}{F}$$

where F_a is the apparent formation factor. The results are summarized in Table 4. The porosities of the samples varied between 38 and 46%. The theoretical value of the formation factor was calculated according to equation (8) using 2.5 and 3 for the densities of clay and sand fractions respectively. The value $k = 4.3$ was used for the shape parameter of the clay particles. These results are shown in Fig. 3 which includes also some of the results obtained by Penman (1940*a*, *b*) using gaseous diffusion. It can be seen in this figure that a fair estimation of the formation factor of a natural soil can be made by applying equation (3) and a k value of 1.9.

TABLE 4.—COMPARISON OF EXPERIMENTAL AND CALCULATED FORMATION FACTORS OF AN ILLITIC SOIL

ϕ	$1/F$	
0.46	0.31	Experimental
0.44	0.28	
0.40	0.26	
0.38	0.26	
0.45	0.26	Calculated

The results given above indicate that the theoretical equations for electric flow through porous media are useful to a great extent in predicting the tortuosity effects in highly complex systems such as natural soils. In conclusion it should be mentioned that we have here considered only fully liquid-saturated soils. The extent to which a species is affected in its mobility in partially saturated soils is obviously greater.

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