

ELECTRICAL CONDUCTIVITY OF Na-MONTMORILLONITE SUSPENSIONS*

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Abstract—The electrical conductivity of Na-montmorillonite suspensions in various salt and clay concentrations was measured. The weight conductance of the clay suspension was found to decrease with increase in clay concentration between 0 and approximately 0.5 g clay/100 ml, then rose to a plateau at 6–10 g clay/100 ml. The weight conductance of the clay suspensions also increased with an increase in the salt solution concentration. If the model of two resistors in parallel is used in interpreting the experimental data, these changes can be attributed to an increase in the mobility of the adsorbed Na ions. It is proposed that the two resistors in series model is more realistic in describing the conductivity of the suspensions. This model predicts the observed weight conductance changes of the suspensions, while the mobility of the adsorbed ions remains constant. A constant mobility of the adsorbed Na ions in clay-water systems of low to medium salt and clay concentrations also is predicted by the diffuse double layer.

INTRODUCTION

Ionic migration in clay systems is involved in such processes as nutrient uptake by plants, soil formation, salination and reclamation of saline soils and many others. One of the convenient ways of determining the ionic mobility is by measuring the electrical conductivity of the clay-water system. Despite its importance, and despite the fact that the electrical conductivity of Na-montmorillonite suspensions has been studied by many workers (Van Olphen, 1957; Van Olphen and Waxman, 1958; Low, 1958; Cremers and Laudelout, 1965; Gast, 1966; Davey and Low, 1968; Jorgensen and Low, 1970), there is still much to be learned. All workers found that there is a rapid drop in the weight conductance of Na-montmorillonite suspensions at a clay concentration range between 0 and 0.5 g/100 ml, but no satisfactory explanation was offered. Van Olphen and Waxman (1958) suggested that this drop may be due to an increase in electrophoretic and relaxation retardation brought about by compression of the electrical double layer as the particles come closer together. This explanation can hardly be applied to 0.5 g clay in 100 ml solution of 10^{-3} N NaCl, where the thickness of the diffuse double layer ($1/K$) is about 100 Å and the average half distance between the clay platelets is 2600 Å. Jorgensen and Low (1970) attributed the drop in weight conductance mainly to a decrease in the fraction of exchangeable Na^+ outside the plane of shear. They did not give any explanation why the fraction of exchangeable Na^+ outside the plane of shear will drop at this very dilute clay concentration.

Between about 0.5 and 6.0 g clay/100 ml there was an increase in weight conductance (Van Olphen, 1957; Van Olphen and Waxman, 1958; Jorgensen and Low, 1970). Van Olphen and Waxman (1958) suggested that at a clay concentration above 0.5 g/100 ml,

the particles start to interact. At this point immobilization of the particles and bridging between the electrodes gradually eliminate the retardation effects and surface conductance takes place. Jorgensen and Low (1970) ascribed this increment in weight conductance to an increase in the fraction of exchangeable Na^+ outside the plane of shear. Again, there was no explanation why the fraction of Na^+ outside the plane of shear increased with further increase of the clay concentration. Both explanations failed to describe quantitatively the increase in weight conductance with clay concentration at the medium clay concentration range.

There is an apparent contradiction between the theoretical prediction and the experimental observation on the effect of electrolyte concentration on the conductivity of clays also. The theoretical prediction was discussed at length by Van Olphen and Waxman (1958). They concluded that since the charge of the clay double layer is determined mainly by imperfections within the clay lattice, the addition of electrolyte does not change the total double layer charge. The counter ion atmosphere is compressed on electrolyte addition and there is a shift of counter ions to the space between the slipping plane and surface; thus, a decrease of the specific surface conductance should take place. In contrast to this prediction, Waxman and Smits (1968), reviewing the abundance of experimental data for the electrical conductivity of shaly formations, observed that in the dilute range of salt concentration there is a sharp increase in conductance with increasing concentration of electrolyte. They attributed this effect to an increase in the mobility of exchangeable ions. Similar measurements on exchange resin (Sauer *et al.*, 1955) and clays (Gast, 1966; Gast and Spalding, 1966; Letey and Klute, 1960) indicated also that addition of a free electrolyte caused a greater increase in electrical conductivity and diffusion rates than that predicted by the increase in the solution conductivity.

The purpose of this study was to find the cause of these contradictions. Electrical conductivity of Na-

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montmorillonite suspensions as functions of clay and electrolyte concentration was measured. The data were analyzed by two different models.

THEORY

The electrical conductance of a clay gel can be considered to be due to the contribution of the colloidal particles and the ions present in solution. In a more schematic way the electrical conductivity can be split up into the contribution of the clay particles and their counter ions (clay conductivity, K_c) and the contribution of the rest of the liquid (K_l). It should be realized that it is rather arbitrary to denote a certain part of the positive ions as counter ions and the rest of them as belonging to the interclay liquid. However, the second method is used mostly in the practice of conductance measurements of colloids.

The major contributor to the conductance of the clay is the excess of ions at the interface of the clay water systems. By definition, the difference between the conductance in the range of the double layer and that in bulk solution is equal to the surface conductance.

The ideal surface conductivity, K_s , can be calculated by multiplying the ionic equivalent conductivity with the surface charge density. For Na-montmorillonite this means

$$K_s = L_{Na} \sigma \quad (1)$$

where K_s is the surface specific conductivity (mho), L_{Na} is the Na equivalent conductivity (mho cm² equiv.⁻¹), and σ is the charge density at the clay surface (equiv. cm⁻²). This calculation is based on the assumption that all sodium ions are distributed on an equipotential surface and their mobility is the same as that in a dilute aqueous solution. The definition is similar to the definition of the equivalent conductivity in salt solution, $\kappa = Lc^*$, where L is the equivalent conductivity, κ is the specific conductivity, and c^* is the concentration of the salt in equivalent per cm³.

The charge density of Na-Wyoming montmorillonite with a cation exchange capacity of 0.90 mequiv./g and specific surface of 750 m²/g, is

$$\begin{aligned} \sigma &= \frac{0.90 \times 10^{-3}}{750 \times 10^4} \text{equiv./cm}^2 \\ &= 1.18 \times 10^{-10} \text{equiv./cm}^2 \end{aligned}$$

Thus, its ideal surface conductance at 25°C is

$$K_s = 50.1 \times 1.18 \times 10^{-10} = 5.9 \times 10^{-9} \text{ mho}$$

The two resistors in parallel model

The clay or the surface conductivity was defined as the difference between the conductance of the interface liquid and the conductance of the interclay solution. This is not an operational definition. In order to separate the experimental conductance of the gel, K_g , into its components—the clay specific conductivity, K_c , and the interclay specific conductivity, K_l —a model must be used. Meredith and Tobias (1962) reviewed and compared the equations developed for the calculation of the electrical conductivity of a mix-

ture from the known conductivities of the separate phases, or vice versa, and found that rigorous solutions were available only for relatively simple cases (dilute suspensions, well-defined shape of the particles, no interaction, etc.). For more complicated systems, like clay gels, equations with empirical parameters should be introduced.

The simplest and most widely used model considers the conductivity cell as consisting of two resistance elements in parallel (Fig. 1a). One component of the cell consists of the electrolyte in the interclay solution and another resulting from the contribution of the clay and the ions adsorbed on it. According to this model (van Olphen and Waxman, 1958; Cremers and Laudelout, 1966; Waxman and Smits, 1968), the electrical conductance of the gel, K_g , is the sum of the surface and solution conductance, namely,

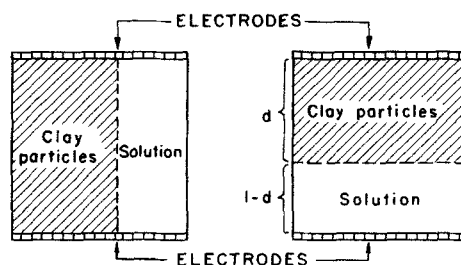
$$K_g = \kappa_c + \kappa_l \quad (2)$$

where K_g is the specific conductivity of the gel, and κ_c and κ_l are the conductances (not specific conductivity) of the clay and interclay solutions, respectively. Based on this model the surface conductivity of the clays may be calculated from the experimentally known electrical conductivities of the gel and the equilibrium solution.

In equation (2), the specific conductivity of the gel is expressed in terms of the conductances of the cell components. In order to express the conductance of the components in terms of their specific conductivity, the geometry of the components and the tortuosity of the paths must be considered. This is usually done by introducing the formation factor, F (Cremers and Laudelout, 1965; Waxman and Smits, 1968), and the resulting equation is

$$K_g = K_c + K_l/F \quad (3)$$

where K_g , K_c , and K_l are the specific conductivities of the gel, clay and liquid phase, respectively. The conductivity of the clay, K_c , can be determined by use of the isoconductivity point method (Dakshinamurti, 1960; Cremers and Laudelout, 1965). If the contribution of the clay conductance is constant, i.e. mobility of the exchangeable ions is constant, and $1/F$ is not influenced by solution and clay concentration, then plotting gel conductivity, K_g , vs solution conductivity, K_l , would form a straight line. From the slope of this line the formation factor is evaluated. The above assumptions do apply to the



Model 1: Resistors in parallel Model 2: Resistors in series
Fig. 1. Resistance models representing the clay particles and the interclay solution. d is the 'thickness' of the clay phase.

electrical conductivity of clay gels at high electrolyte concentrations and equation (3) was used by Cremers and Laudelout (1966), Cremers *et al.* (1966) and Waxman and Smits (1968) to calculate the formation factors of their system.

The two-resistors-in-parallel model was applied in the following sections to analyze the experimental results.

EXPERIMENTAL PROCEDURE

A clay size fraction of Upton Wyoming montmorillonite (API No. 25) was obtained by allowing large size fractions to settle out of suspension and then siphoning off the suspension. Homoionic Na-clay was prepared by saturating the colloid fraction with normal NaCl solutions. This treatment was repeated four times. Thereafter, the clay was washed with distilled water in a high-speed centrifuge until tests with AgNO_3 indicated that the equilibrium solution was free of chloride. Then the clay was washed once more and the salt-free gel was freeze-dried and stored.

The suspension was prepared by mixing known weights of dry clay with equal volumes of NaCl solutions of various initial concentrations. Seven concentrations of clay in the suspensions (0.1, 0.25, 0.5, 1.0, 2.5, 6.0 and 8.0 per cent by weight) and three NaCl solutions (1×10^{-4} , 1×10^{-3} and 3×10^{-3} N) were studied. In order to determine the isoconductivity value and the formation factor of this clay, the electrical conductivities of two suspensions (1.0 and 2.5 per cent by weight) in nine NaCl solutions (0.0001, 0.001, 0.003, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 N) were examined.

The electrical conductivity of the solutions and of the suspensions was determined with a Pyrex glass dip cell (Yellow Springs Instrument Co., YSI 3400) and a conductivity bridge (Industrial Instruments Inc., model RC 16 B2). The electrical conductivity of suspensions that were equilibrated for 24 hr (at 25°C) was measured. After the conductivity of the suspensions was measured, the suspensions were centrifuged in a high-speed centrifuge, and the conductivity of the supernatant solution, K_i , was determined.

RESULTS AND DISCUSSION

1. Effect of electrolyte concentration

(i) *The formation factor.* The specific conductivity of 1.0 and 2.5 per cent Na-montmorillonite suspensions as a function of the conductivity of NaCl solutions is presented in Fig. 2. It is evident that in both suspensions there is an initial rapid increase in gell conductance which is greater than the conductivity of the added electrolyte alone. However, at the higher salt concentrations, a linear relation between the two axes is obtained with slopes of 0.885 and 0.81 for the 1.0 and 2.5 per cent clay, respectively. The corresponding F values (equation 3), are 1.13 and 1.235, respectively.

Following Cremers and Laudelout (1966) and Cremers, Van Loon and Laudelout (1966), the formation factor is related to the porosity, ϕ , in the follow-

ing way:

$$F = 1 + k \left(\frac{1 - \phi}{\phi} \right) \quad (4)$$

where k is a parameter which depends on the axial ratios of the solid particles. The values of k , as calculated from equation 4, are 26 and 24 for the 1.0 and 2.5 per cent clay, respectively. These values are intermediate between the values of $k = 13.9$ obtained by Cremers and Laudelout (1966), and the value of $k = 52.9$ obtained by Gast and Spalding (1966).

(ii) *The isoconductivity point.* When the electrical conductivity of a clay gel, K_g is compared to that of the solution, K_i , it is found that at low electrolyte concentration, the conductivity of the gel is higher than that of the interclay solution. At high concentrations of salt the opposite is true and the conductivity of the electrolyte solution is higher than that of the gel. The relatively lower conductivity of the gel in the systems of high salt concentration is caused by interactions of electrolyte and water with the clay surfaces and the tortuosity of the paths. Conversely, when the electrolyte concentration is low, the contribution of the adsorbed ions and the clay macroions to the conductivity of the gel is more effective than the reduction in the salt conductivity, so that K_g is higher than K_i . These relations are presented in Fig. 3. The conductivity at which both effects balance each other, namely when the gel conductivity is equal to the conductivity of the interclay solution, is called the isoconductivity point (Dakshinamurti, 1960; Cremers and Laudelout, 1965). As is evident from Fig. 3, the isoconductivity point of Na-Wyoming montmorillonite is 2.65 m mho/cm. This value agrees with the values reported in the literature (Dakshinamurti, 1960; Cremers and Laudelout, 1965 and 1966).

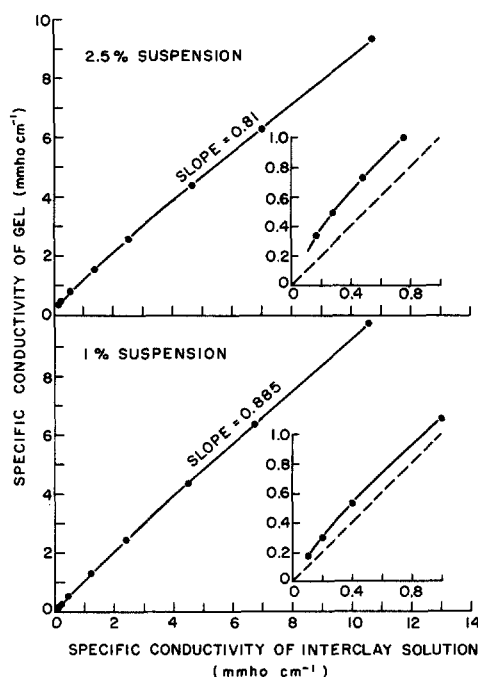


Fig. 2. Specific conductivity of Na-bentonite suspensions vs specific conductivity of interclay solution, 1 and 2.5 per cent suspensions.

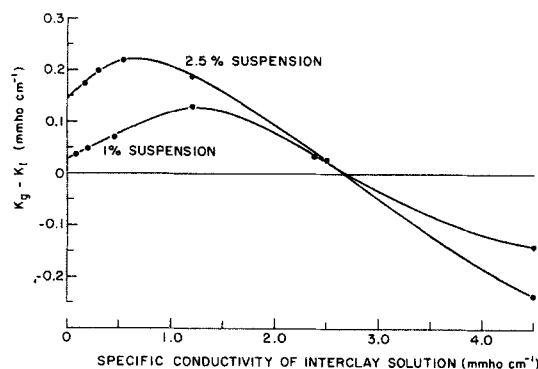


Fig. 3. Difference between specific conductivity of the suspension and interclay solution vs the specific conductivity of the inter-clay solution.

Following Cremers and Laudelout (1965) the surface specific conductivity, K_s , can be calculated from the isoconductivity point, K_{iso} , according to the equation

$$K_{iso} = \frac{2.65 K_s S_o}{k} \quad (5)$$

where S_o is the specific surface area of the clay and 2.65 is the density of the clay (note that K_{iso} is equivalent to K_o). Substituting the value for k obtained in the previous section, one has

$$K_s = \frac{25 \times 2.65 \times 10^{-3}}{2.65 \times 7.5 \times 10^6} = 3.33 \times 10^{-9} \Omega^{-1}$$

which is 0.56 of the ideal value for the surface conductivity of Na-montmorillonite as calculated in the introduction. This value is in agreement with the values obtained by Van Olphen (1957), Gast (1963), Shainberg and Kemper (1966a), and Low (1968). It is also in reasonable agreement with the portion of adsorbed ions not residing directly on the surface, as calculated by Shainberg and Kemper (1966b), considering both hydration and electrical potential energies in the Boltzmann distribution equation.

II. Effect of clay concentration

The effect of clay concentration on the conductivity of the suspension is best denoted when the weight conductance is plotted as a function of clay concentrations. The weight conductance is determined by the difference between the conductivity of the gel and that of the original solution, divided by the concentration of the clay in g/100 ml (van Olphen and Waxman, 1958), (Fig. 4, upper part). The weight conductance-concentration curves appear to have the same general shape as those reported by van Olphen (1957), van Olphen and Waxman (1958), Gast (1966) and Jorgensen and Low (1970). There is a rapid drop in the weight conductance at a clay concentration up to 0.5 g/100 ml followed by an increase in weight conductance up to concentration of 6 g clay/100 ml suspension.

It is known (Brown and Miller, 1971; Shainberg, 1973) that aqueous Na-montmorillonite suspensions are not stable and hydrolyze even in dilute salt solutions. As a result of this reaction, the conductivity of the interclay solution increases above that of the

solution used for preparing the suspension. This increase is due to salt exclusion from the clay surface also (Shainberg and Kaiserman, 1967). The increase in conductivity of the interstitial solution above that of the original solution is presented in Fig. 5 (lower part). In calculating the weight conductance the difference between the conductivity of the clay suspension, K_g , and that of the original solution, K_o , is usually used (Fig. 5, upper part). As can be seen from Fig. 5 (upper part), this difference ($K_g - K_o$) is larger than the real difference existing in the suspension. In order to present the results in a more realistic form, the weight conductance was calculated by using the difference between the suspension conductivity, K_g , and the interclay solution conductivity, K_l (Fig. 4, lower part).

It is evident that the drop in the weight conductance-concentration curve was eliminated. The drop in the weight conductance at the low range of clay concentration reported by many workers was probably an artifact resulting from the way of calculating the weight conductance, which did not take into account the instability of the clay in dilute clay suspensions. The contribution of the soluble decomposition products was probably exaggerated because it was divided by the clay concentration and resulted in an increase in the weight conductance of the clay as the clay concentration decreased.

However, above 0.5 per cent clay the increase in the weight conductance with increase in salt and clay concentration is still obtained even if the electrical conductivity of the interclay solution is taken into account. To explain this one has to consider the two-resistors-in-series model.

Two-resistors-in-series model

Other models to describe the conductivity of clay water systems were used by Spiegler *et al.* (1956), Fripiat *et al.* (1965) and Gast (1966). Fripiat's model con-

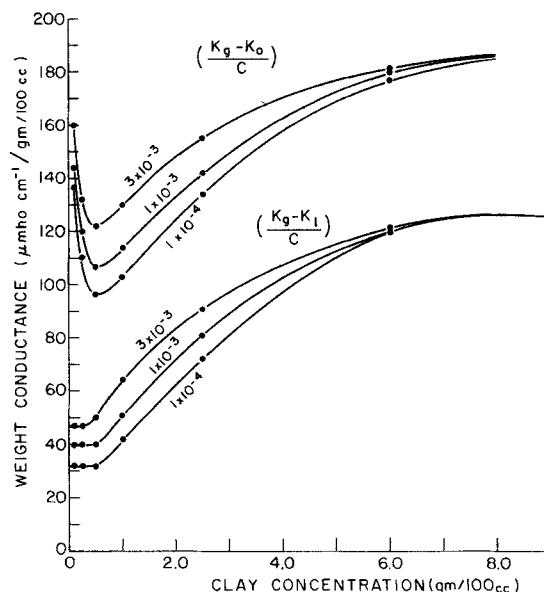


Fig. 4. Weight conductivity of Na-bentonite vs clay concentration.

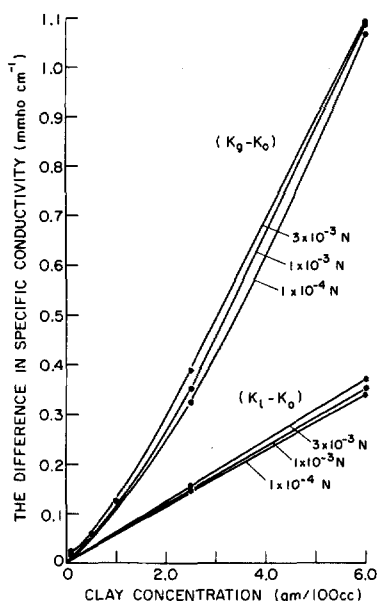


Fig. 5. Differences between specific conductivities of suspensions K_g and original solutions, K_o , and between inter-clay solution, K_i , and original solutions, K_o , vs clay concentration, for three solution concentrations.

sists of two resistance elements, the clay and the inter-clay solution, in series (Fig. 1b), while Gast used the model proposed by Spiegler *et al.* (1956), consisting of three components in parallel, one of which has its elements in series.

Based on the two resistors in series model the specific resistance of the gel, in Ω , is the sum of the resistances of the elements,

$$R_g = \rho_c + \rho_l \tag{6}$$

where ρ_c and ρ_l are the resistances of the clay and the interstitial liquid, respectively. The specific resistance of the clay, R_c , and the liquid R_l , are given by Ohm's law.

$$\rho_c = R_c d \quad \text{and} \quad \rho_l = R_l(1 - d) \tag{7}$$

where d is the length parameter corresponding to the "thickness" of the clay phase (Fig. 1b).

The specific conductivity of the gel is given by

$$K_g = \frac{1}{R_g} = \frac{1}{\rho_c + \rho_l} = \frac{1}{R_c d + R_l(1 - d)} = \frac{K_c K_l}{K_l d + K_c(1 - d)} \tag{8}$$

If one knows the specific conductivity of the clay particles as calculated from the isoconductivity value, then the electrical conductivity of the gel as a function of the specific conductivity of the interclay solution may be calculated for various clay concentrations, namely, various d values. Similarly, the effect of the clay concentration, d , on the conductivity of the gel (for a given interclay solution), may also be calculated. The results of these calculations are presented in Figs. 6 and 7.

In Fig. 6, the specific conductivity of the gel, K_g , as a function of the solution conductivity, K_i , was calculated using equation (8) and the value for the

specific conductivity of the clay, K_c , as determined from the isoconductivity point. It is evident from Fig. 6 that, at the low range of salt concentration, the increase in the specific conductivity of the equilibrium solution results in a greater increase in the conductivity of the gel. This is in line with our experimental results (Figures 2, 4 and 5) and the results reported in the literature (Waxman and Smits, 1968). It is clear that this is a natural outcome of the model, which at the range of low salt concentration describes the clay-water system more realistically, and it was not necessary to conclude that the mobility of adsorbed ions increases with an increase in the solution concentration.

Comparing the experimental results (Figs. 2, 3 and 5) with the curves in Figure 6, one should note that the data of the 1.0 per cent suspension lies on the curve of $d = 0.2$, the data points of the 2.5 per cent clay lie on the curve of $d = 0.5$ up to $K_i = 0.5$ m mho; thereafter, the data points move in the direction of the $d = 0.2$ curve. Similarly, the data points of 6 per cent clay suspensions coincide with the $d = 0.8$ curve up to $K_i = 0.5$ m mho; thereafter, they deviate in the direction of the $d = 0.5$ curve.

The volumetric fraction of the clay at the 1.0, 2.5 and 6.0 per cent by weight suspension is about 0.004, 0.01 and 0.024, respectively. Comparing the volumetric fraction of the clay particles with the volumetric fraction of the clay resistors in the model ($d = 0.2, 0.5$ and 0.8 , respectively), it is evident that the "thickness" of the clay should include part of the diffuse double layer at each clay-water interface. At the low range of salt concentration ($< 0.5 \times 10^{-3}$ N), the ratio between the thickness of the clay platelets with the ionic atmosphere and that of the platelets themselves is between 33 and 50, which corresponds to diffuse double layer thickness of 150 to 250 Å. As the salt concentration increases, the 'thickness' of the ionic atmosphere decreases and the experimental curves move from a predicted curve of high d value to a curve with a lower d value. The 'thickness' of the clay phase, d , is a function of both clay and electrolyte concentrations. For a given electrolyte con-

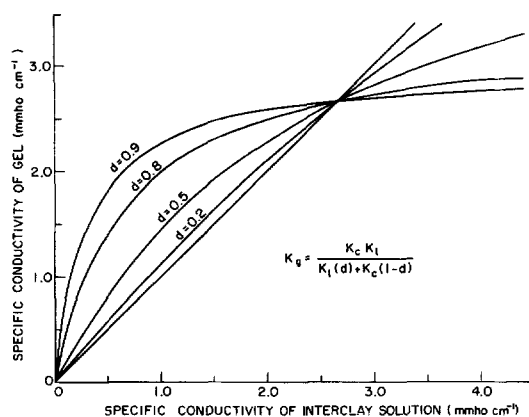


Fig. 6. Specific conductivity of Na-bentonite gels vs specific conductivity of interclay solution (calculated from the two-resistors-in-series model and assuming $K_c = 2.65$ m mho cm^{-1}).

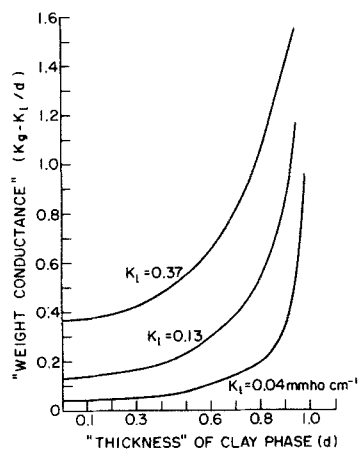


Fig. 7. "Weight Conductance" of Na-bentonite vs the "thickness" of the clay phase (calculated from the two-resistors-in-series model).

centration, d increases with an increase in clay concentration. For a given clay concentration, d decreases with an increase in electrolyte concentration.

The 'weight conductance' of the clay as calculated from equation (8) is

$$\frac{K_g - K_l}{d} = \frac{K_l(K_c - K_l)}{K_l d + K_c(1 - d)} \quad (9)$$

where d , the 'thickness' of the clay resistor, is proportional to the clay concentration. Substituting the experimental value for K_c ($= 2.65 \text{ m mho cm}^{-1}$), the new 'weight conductance' may be calculated as function of d (proportional to the clay concentration) for various values of the equilibrium solution conductivity. The results of these calculations are presented in Figure 7. It is evident that at a low clay concentration there is no change in the "weight conductance" of the clay with an increase in the clay concentration. This prediction is in agreement with our experimental observation (Figure 4). As the concentration of the clay increases, the two-resistors-in-series model predicts an increase in the "weight conductance", in agreement with the experimental observation. We conclude that the two-resistors-in-series model may account for all the experimental observations without the need to assume that the surface conductivity of the clay increases either with an increase in clay or solution concentration.

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