

# SURFACE CONDUCTANCE OF SODIUM BENTONITE IN WATER<sup>1</sup>

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## ABSTRACT

The concept of surface conductance and its role in the interpretation of the formation resistivity factor of reservoir rocks is reviewed.

The specific surface conductance of a clay is determined for four narrow particle-size fractions of sodium Wyoming bentonite in conductivity water. The values are derived from the specific conductance of gels of these clays on the basis of the picture of an idealized cubic network structure of the clay plates. The average surface conductance for internal and external surfaces of the bentonites is found to be  $3.2 \times 10^{-9} \text{ ohm}^{-1}$ , which is  $0.55 \times$  the value expected when all exchangeable ions are assigned their infinite dilution mobility. The data are independent of particle size.

In addition, conductivity data are presented for clay suspensions in a wide range of concentrations. In extremely dilute suspensions, the contribution of the clay to the conductivity when expressed per unit weight of clay (the so-called "weight conductance") is smaller than expected from an independent movement of particle and counter ions. This is interpreted to be partly a result of both electrophoretic and relaxation retardation, indicating that the electrical double layer on sodium bentonite has a condensed character. Probably part of the counter ions are entirely immobilized by adsorption on the surface.

With increasing clay concentration, further compression of the double layer increases the retardation effects and a further decrease of the weight conductance is observed. A minimum is reached at a concentration of a few tenths of one percent clay at which, according to viscosity and light absorption data, particle interaction becomes apparent. At this point, immobilization of the particles and bridging between the electrodes gradually eliminate the retardation effects, and surface conductance takes over. The weight conductance increases gradually until a constant value is reached in a concentration range of 5 to 12 g of clay per 100 ml gel, from which the above value of the specific surface conductance was computed.

## INTRODUCTION

In petrophysics, a useful parameter for the characterization of rocks is the so-called "Formation Resistivity Factor,"  $F$ . The factor is defined as the ratio of the specific resistance of a porous rock filled with fluid to the specific resistance of the fluid contained in the pores. The factor  $F$ , measured under specified conditions, can be correlated with the porosity  $f$  of the rock.

In many rocks the formation resistivity factor is a function of the specific resistance of the pore fluid. Originally (Patnode and Wyllie, 1950) this function was interpreted by assuming that the rock and the pore fluid could be consid-

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ered parallel conductors, and the following equation was used:<sup>1</sup>

$$\kappa(\text{rock plus fluid}) = \kappa(\text{rock}) + \kappa(\text{fluid}) \quad (1)$$

Soon it was recognized, however, that the conductance of the rock when filled with fluid is not determined by the conductance of the bulk rock material, but rather by the relatively high conductance of the interface between the rock and the pore fluid (Winsauer and McCardell, 1953). At this interface an ionic double layer exists: The rock surface is usually negatively charged and, in the solution opposite this negative surface, cations are accumulated to restore electroneutrality. The excess of cations close to the rock surface over the number of cations in the bulk of the fluid is responsible for an excess conductance along the rock surface over the bulk fluid conductance. This excess conductance is called the "surface conductance."

Consequently, only in each single pore or section of a pore may the rock surface and the pore fluid be considered parallel conductors. For each section of a pore, therefore, the following equation holds:

$$\kappa(\text{fluid-filled pore}) = \kappa(\text{rock surface}) + \kappa(\text{pore fluid}) \quad (2)$$

It can be shown that equation (1) does not necessarily follow from equation (2) when the pore geometry is taken into account. Thus equation (2) rather than (1) should be taken as a basis for the interpretation of the relation between the formation resistivity factor and the pore-fluid resistivity. In the analysis of this relation two factors should be discussed: the pore geometry and the relative magnitude of the surface conductance with respect to the bulk-fluid conductance. Also a possible dependence of both pore geometry and specific surface conductance on the salt content of the fluid in the pores should be considered.

The purpose of the present paper is to evaluate the magnitude of surface conductance. For the rock material, bentonite clay was chosen since this material was expected to show rather pronounced effects owing to its large surface area and high electric double-layer charge.

A brief review of the theory of surface conductance is given first.

### *Acknowledgment*

The authors wish to acknowledge the experimental assistance of C. T. Deeds.

<sup>1</sup> The terms "conductance" ( $\kappa$ ) and "resistance" ( $\rho$ ) indicate values for systems of any geometry. They are a function of the cell constant of the system and the fundamental properties "specific conductance" ( $K$ ) and "specific resistance" ( $R$ ). In logging engineering the latter terms are usually called "conductivity" and "resistivity."

The practical units for conductance and resistance are the mho and the ohm and for specific conductance and resistance mho-cm<sup>-1</sup> or mho-m<sup>-1</sup> and ohm-cm or ohm-m, the cell constant having the dimensions of (length)/(cross sectional area)  $\sim l^{-1}$ .

In the case of surface conductance, however, the cell constant has the dimension of (length)/(cross sectional length) and therefore surface conductance as well as the specific surface conductance are measured in mhos.

## THEORY OF SURFACE CONDUCTANCE

The theory of surface conductance (or "double-layer conductance") has been given by several authors (Cole, 1933; Bikerman, 1935; see also Kruyt, 1952, p. 235–238). Briefly, the reasoning is as follows:

In the fluid part of the electrical double layer opposite a negatively charged surface, there is an excess of positive ionic charge, or, stated more precisely, an excess of cations and a shortage of anions as compared with the ionic concentrations far from the surface in the bulk of the electrolyte solution. By definition, the *difference* between the conductance in the range of the double layer and that in the bulk fluid is equal to the surface conductance.

It is assumed in the theory that only that fraction of the ions in the double layer which is mobile in electrokinetic experiments participates in the transport of electricity. This means that the ions located in the space between the electrokinetic "slipping plane" and the surface (which includes the "Stern" part of the double layer) are considered immobile.

A second assumption is that both the participating double-layer ions and the ions in the bulk solution may be assigned their infinite dilution mobility.

If electroendosmosis develops (in dc, not in high-frequency ac), the ion mobilities in the region of the double layer should be corrected by adding the electroendosmotic mobility to the cation mobility and subtracting it from the anion mobility if the surface is negatively charged.

The theory gives a relation between specific surface conductance and the zeta potential and electrolyte concentration. For glass in pure water or in extremely dilute electrolytes a specific surface conductance of the order of  $10^{-9}$  ohm<sup>-1</sup> is predicted, based on the observed zeta potentials.

Almost all the experimental data for surface conductance in the literature are for the system glass/electrolyte solution. The reported values vary appreciably: from  $10^{-9}$  up to  $10^{-7}$  ohm<sup>-1</sup>. This may be attributed partly to the variation in the composition of the glasses used, but for the greater part experimental difficulties are responsible for the discrepancies. The main problem, experimentally, is to obtain systems of simple and known geometry with a large surface area with respect to bulk volume. In a cylindrical capillary, for example, the measured total conductance is the sum of the surface-conductance contribution  $\kappa_s = (\pi d/L) K_s$  and the bulk-fluid-conductance contribution  $\kappa_w = (\frac{1}{4}\pi d^2/L) K_w$  (if  $L$  is the length and  $d$  the diameter of the capillary). Surface conductance can be determined with reasonable accuracy only if surface and bulk conductance are of the same order, that is, if  $\frac{1}{4}dK_w = K_s$ . If almost pure water is used with a conductivity of  $10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup> and  $K_s$  is of the order of  $10^{-9}$  ohm<sup>-1</sup>, a capillary of the radius of 20 microns is required. For higher electrolyte concentrations, much smaller capillaries must be used to obtain reasonable accuracy.

The latest and most reliable experimental data in the lower electrolyte concentration range agree with the theoretical prediction, and hence the assumptions made in the theory may indeed be valid for the double layer on glass.

Glass as well as silica in general has a well-developed diffuse double layer with no indication of specific adsorption forces between surface and counter ions.

In regard to clays, however, it has been concluded from earlier work on the flat double-layer interaction (van Olphen, 1954) that a considerable part of the cations would be fixed in the Stern layer by specific adsorption forces. Part of the counter ions are even located in the 10-Å spacing between the unit layers of the particles, and one might wonder whether these ions are still able to move in an electrical field parallel to the surface. Therefore, there is no way to extrapolate from the data for glass, where most counter ions are in the diffuse Gouy layer, to clays where the majority are in the Stern layer. Only the measurement of the surface conductance of clay may supply an answer.

Another basic difference between the double layers on glass or sand and those on clays should be considered when discussing the effect of electrolytes on the surface conductance of these two materials:

In the interpretation of the formation resistivity factor of porous rocks and its dependence on the electrolyte concentration in the pores, two factors are important, as mentioned previously: (1) the effect of possible changes in pore geometry, affecting the "cell constants" of the rock and therefore the relative contribution of surface conductance; and (2) the effect of a possible change of the *specific* surface conductance with electrolyte concentration in the pores. The latter will be discussed now in more detail.

As the range of electrolyte concentrations in which reliable experimental data can be obtained is rather limited, one has to rely to a great extent on theoretical speculation. Fortunately, the contribution of surface conductance to the total conductance of the core becomes of less importance with increasing electrolyte concentration if the pores are not very small.

If we restrict the discussion first to surfaces of glass or of sand grains—which are closely analogous—the following effect of electrolytes on the specific surface conductance may be anticipated.

The theory of surface conductance shows that the increase in specific surface conductance should be proportional to the square root of the electrolyte concentration  $c$ . This is because the double-layer charge increases in proportion to  $\sqrt{c}$ , according to the double-layer theory for surfaces of the silica type. Simultaneously, however, the zeta potential decreases with increasing electrolyte concentration. This is due to a compression of the double layer, resulting in a shift of the counter ions from the diffuse part of the double layer to the space between the surface and the slipping plane. The resulting reduction of the surface conductance largely compensates the increase due to the increase in charge with  $\sqrt{c}$ : On the basis of the observed reduction of the zeta potential of glass the computed surface conductance is expected to increase by a factor of only 5 when the electrolyte concentration increases by a factor of  $10^4$ . If, more correctly, the electrolyte concentration is substituted by the activity, a factor smaller than 5 will be anticipated. Such small changes of surface conductance

with electrolyte concentration are indeed shown by the experimental values in the range of extremely low electrolyte concentrations, where they can be measured.

It is emphasized that this discussion is valid for such surfaces as those of glass and sand grains. Clay has not been mentioned because the double layer on the clay surfaces has a basically different character. This difference is (apart from the specific Stern adsorption forces mentioned above) that the silica double layer has a varying charge, whereas the charge of the clay surface is a constant independent of the electrolyte concentration. This is another reason why the data for glass cannot be extrapolated to clay.

The glass surface obtains its negative charge by the adsorption of so-called potential-determining ions which are possibly OH ions. An equivalent amount of cations, for example H ions, make up the diffuse counter-ion atmosphere. The total potential difference between the negative surface and the solution far from the surface outside the diffuse double layer is thermodynamically determined by the activity of the "potential determining" OH ions. This potential is the Nernst potential, and, as it does not change on addition of indifferent electrolyte, the glass double layer is called a "*constant potential*" double layer although, of course, the electrokinetic zeta potential does decrease with electrolyte addition. However, the total charge of the double layer increases with electrolyte concentration proportional to  $\sqrt{c}$ . (Of course, this holds true only if there are enough OH ions available to increase the surface charge; this is realized in dilute suspensions but in narrow capillaries it may be necessary to flush with several "pore" volumes in order to supply a sufficient amount of OH ions.)

The charge of the clay double layer, on the other hand, is entirely determined by imperfections within the clay lattice. For example, trivalent aluminum may be replaced by divalent magnesium, resulting in a shortage of positive charge, and the lattice becomes negatively charged. In order to retain electroneutrality, this negative lattice charge is compensated by the accumulation of cations opposite the outer surfaces of the clay, and these cations always remain combined with the clay during drying and resuspension. These are the exchangeable ions that constitute the counter-ion atmosphere of the double layer. The addition of electrolyte does not change the total double-layer charge, and therefore this is called a "*constant charge*" double layer. However, the counter-ion atmosphere will be compressed on electrolyte addition and there will be a shift of counter ions to the space between slipping plane and surface. If this shift indeed reduces the average mobility of the counter ions, a decrease of the specific surface conductance should be expected, and in this case there is no compensating increase as there is no increase in charge. Therefore, if there is any change in specific surface conductance of clay with electrolyte concentration, this change cannot be an increase, as for glass, but must be a decrease.

These considerations apply to the double layer on the flat surfaces of the clay plates. The contribution of the double layers on the broken edges may be ex-

pected to be negligible because of the relatively small edge-surface area.

The difference in character between the silica and the clay double layer should always be kept in mind when comparing the properties of sand and clay. This distinction was, for example, not made by Winsauer and McCardell (1953), who treated the clay double layer as a constant potential rather than a constant charge double layer and stated that clay conducts only in an ionic solution from which it can adsorb negative ions to build up the inner sheet of the double layer, opposite which cations are accumulated.

Summarizing, the specific surface conductance of sand may be anticipated to increase somewhat with increasing electrolyte concentration, and that of clay may be expected to decrease a little.

Only data for the surface conductance of clay in pure water are given in the present study; the effect of electrolyte concentration in the range where the relative surface-conductance contribution is still large enough to be measurable has not yet been investigated.

## DETERMINATION OF THE SURFACE CONDUCTANCE OF BENTONITE

### *Experimental Approach*

In order to determine the surface conductance of a material, a system of known surface area and of simple geometry is required. The difficulty of obtaining such a system in microcrystalline materials such as clays has been the main obstacle to progress in surface-conductance work. This explains why practically all the available data are for glass, which can be made into capillaries.

In electrochemical or electrokinetic work, microcrystalline materials are often made into porous granular plugs, but this introduces all the unknown effects of pore geometry with which one is faced in the interpretation of the electrical properties of rock formations.

Fortunately, in the case of clays, we can prepare homogeneous gels that may adequately suit the purpose. From previous work on clay gels (van Olphen, 1956) it seems reasonable to visualize the structure of such a gel as a cubic scaffolding of square clay plates. Therefore, the derivation of clay surface conductance from data for the conductivity of homogeneous clay gels on the basis of this idealized picture seems realistic and worth the effort. Variation of both the clay concentration and the particle size should be helpful in the analysis of the gel conductivity data.

In addition it was considered desirable to investigate the contribution to the conductivity by individual clay particles which may be measured in dilute clay suspensions.

Hence it was decided to determine the conductance of clay suspensions of various size fractions in a wide range of clay concentrations, including dilute suspensions of 0.005 g/100 ml up to rigid gels of about 12 g/ml.

All this work had to be carried out with a monoionic clay. Sodium bentonite was chosen for the study reported here, but the work will be extended to calcium

and hydrogen clay in order to investigate the effect of variation of both the mobility and the valence of the exchangeable ion.

For a discussion of previous literature on the conductance of clay suspensions, Chapter 10 of Marshall's (1949) book and the list of references on his page 119 may be consulted.

#### *Preparation of Systems*

A suspension was made of about 1 percent natural Wyoming bentonite in deionized water. Coarse, mainly nonclay matter was allowed to settle and was separated from the clay fraction by decantation. To convert the clay to the sodium form, the decanted suspension was repeatedly passed through a column that was packed with Dowex-50 resin in the sodium form. The resulting sodium clay suspension was washed with deionized water by repeated centrifuging and resuspending, using the "Spinco" preparative ultracentrifuge. Then, in the same centrifuge, the suspension was separated into five rather narrow size fractions which were labeled R-1 to R-5 according to decreasing average particle size (see also Kahn and Lewis, 1954).

The clay content of each fraction was determined by weighing the clay after drying a portion of the suspension to constant weight at 105°C. The concentration of the suspensions of the five fractions was between 2 and 3 g/100 ml. These suspensions were diluted with deionized water to obtain a series of different concentrations ranging from 0.005 to 3 g/100 ml. More concentrated gels were prepared by ultracentrifuging these suspensions and decanting the supernatant liquid. In this way air-free gels were obtained which could be transferred to a special conductivity cell with the least possible disturbance. During the process of centrifugation there is some sorting of size, and the resulting sediment will not be perfectly homogeneous. However, as will be shown later, the conductivity of the concentrated gels is independent of particle size so that the slight inhomogeneities will not affect the final results. The concentration of each of these gels was determined separately by weighing a portion of the gel and drying it to constant weight at 105°C. From this the concentration was found in grams per 100 grams of gel, which may be called  $a$ . The concentration in terms of grams per 100 ml gel, which is required in conductivity work, was calculated from the following formula:

$$c = 100a / [(a/2.7) - 100 - a] \text{ grams/100 ml}$$

where 2.7 is the density of the dry clay and 1.0 the density of the water; this neglects the small correction that would be needed if the density of the inter-layer water of the bentonite were different from 1.

The following data for the base-exchange capacity of the five sodium bentonite fractions were obtained by converting to the ammonium form, washing, and measuring the nitrogen content of the ammonium clays:

R-1 : 74 ; R-2 : 89 ; R-3 : 92 ; R-4 : 87 ; R-5 : 91 meq/100 g.

The low figure for the R-1 fraction suggested that probably there was still some nonclay material left in this fraction, and this fraction was therefore discarded.



Spectrochemical analysis showed that there was no more than 0.35 meq/100 g of calcium present, which amounts to about 0.4 percent of the base-exchange capacity. No potassium could be detected.

### *Conductivity Measurements*

Resistance values were determined with a Campbell-Shackelton Shielded Ratio Box (Behr and Williams, 1932), Cat. no. 1553, Leeds and Northrup Co., Philadelphia, Pa., together with accessory equipment. The balance point was indicated by a Cathode Ray Oscillograph, Model 304-A, Du Mont Laboratories Inc., Clifton, N. J. Accessory equipment for the high-frequency measurements included a Hewlett-Packard Oscillator, Model 650-A and a DC Decade Amplifier, Model 103, Kay Lab, San Diego, Calif. The over-all limit of error of the bridge was 0.1 percent. The Decade Box was checked with a noninductive carbon resistor at 50 kilocycles/second.

The following conductivity cells were used:

For clay suspensions up to about 2 to 3 percent, a Pyrex glass dip cell—Cat. no. CEL BB1, Industrial Instruments Inc., Cedar Grove, N. J., cell constant about 1.0, or alternatively a Jones conductivity cell—Cat. no. 4943-A, Leeds and Northrup Co., cell constant about 0.25.

For rigid clay gels, a specially designed Plexiglas cell (Fig. 1) was used—one has a cylindrical bore, length 20 mm, diameter 5 mm; the other has a square

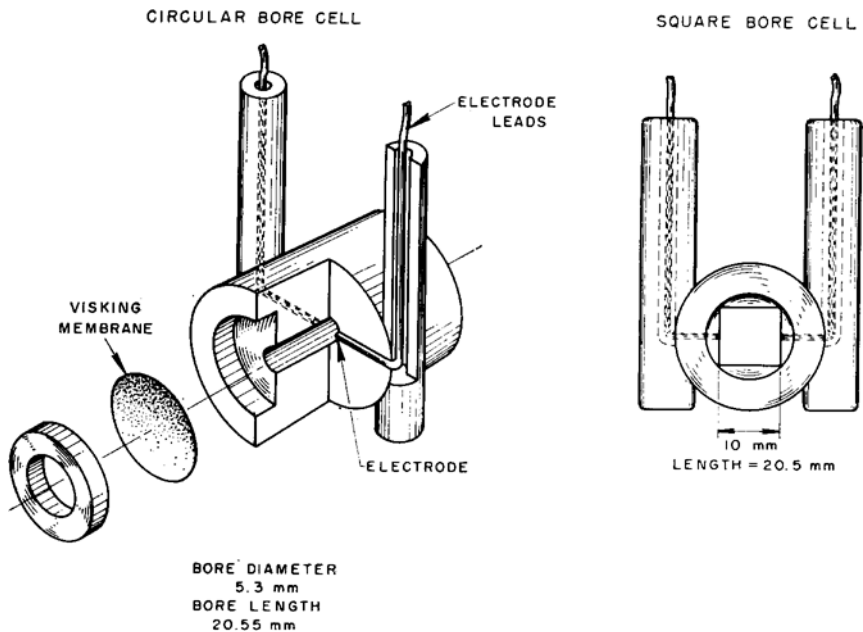


FIGURE 1. — Plexiglas conductivity cells for clay gels.



bore, length 20 mm and cross section  $10 \times 10$  mm. The electrodes are round platinum wires of 1.5 mm diameter, which are rigidly fixed in the Plexiglas diametrically opposite each other and cut off flush with the wall of the bore. A sample of the centrifuged gel was taken from the centrifuge tube with a glass tube of slightly larger bore than that of the cell. Then the gel was pushed from the glass tube into the cell, avoiding inclusion of any air. Excess gel was removed flush with the bore, and then the gel was restrained between electrochemically inert Visking sheets.<sup>1</sup> The core holders were then clamped between Plexiglas chambers filled with distilled water. The cell constants of these cells were of the order of 8.0.

All the cells were calibrated in various resistance ranges and at frequencies between 2 and 50 kilocycles/second, and the slight variations in the cell constants were taken into account in the measurements on the clay suspensions. Except for the very dilute solutions there was practically no dependence of the cell constant on frequency for the dip cell and the Jones cell. For the Plexiglas cells there was an appreciable frequency dependence. For the square bore cell, for example, the frequency dependence in the resistance range of the gels was as follows:

Frequency:	2	10	20	40	50 kilocycles/sec
Cell Constant:	8.37	8.00	7.89	7.82	7.79

The resistance measurements with either the dip cell or the Jones cell were made in an oil bath, thermostated at  $25.00^\circ\text{C}$  plus or minus  $0.01^\circ\text{C}$ . When the Plexiglas cells were used the temperature of the system was measured and the resistance was then corrected to  $25.0^\circ\text{C}$ , applying a temperature coefficient of 2 percent per degree C for the conductivity. Room temperature varied from  $21^\circ$  to  $24^\circ\text{C}$ .

### Results

In Figure 2 the results of the conductivity measurements are given in terms of  $K_c/c$  as a function of  $\sqrt{c}$ .

In analogy with equivalent conductance,  $K_c/c$  was called the "weight conductance" of the clay in the suspension. The values were obtained as follows: The contribution of the clay to the conductance of the suspension was found by subtracting the specific conductance of the water that was used for the dilutions from the specific conductance of the suspension. This difference is called  $K_c$ , which is then divided by the concentration in g/100 ml to obtain the "weight conductance."

In the extremely low concentration range from 0.005 to 0.10 g/100 ml the conductance of the water is a rather large fraction of the total conductance so that the variations in the conductance of the water that are due to contact with air during handling of the dilutions cause rather large errors in the calculated weight conductance of the clay. In Figure 3 the specific conductance of the suspension is plotted versus the clay concentration in this range for all four fractions. A line is drawn through the averages for the four fractions at each con-

<sup>1</sup> Product of the Visking Corp., Chicago, Ill.

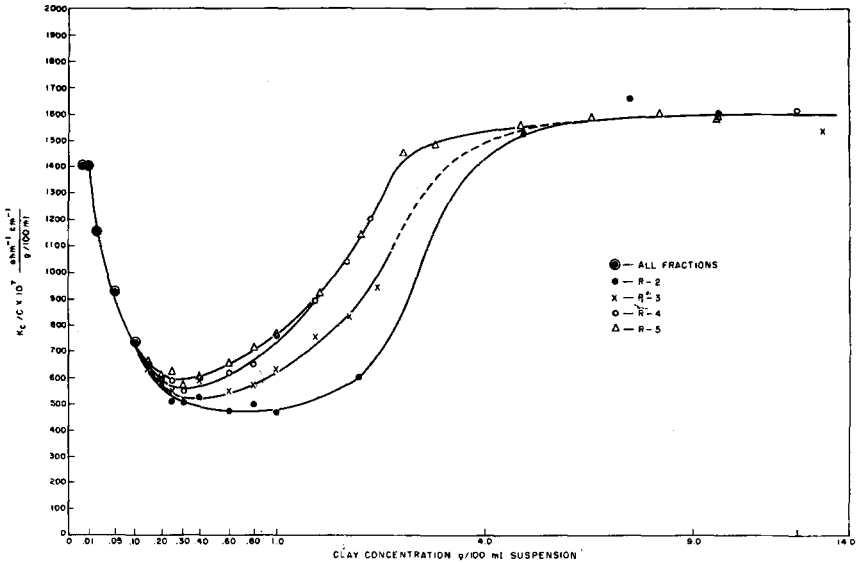


FIGURE 2.— $K_s/c$  as a function of the clay concentration (plotted as  $\sqrt{c}$ ) for four size fractions of sodium bentonite at 25°C.

centration, which is extrapolated to zero concentration. The extrapolated specific conductance of the make-up water of  $7 \times 10^{-7}$  ohm $^{-1}$  cm $^{-1}$  is actually a good average for the water used. On inspection of the positions of the individual points with respect to the average curve it is apparent that the average curve is a fair representation of all four individual curves and it irones out some scatter of individual points.

There appeared to be little frequency dependence of the conductivity in the range of 2 to 50 kilocycles/second. Only in the concentration range of 0.3 to 2.5 g/100 ml was there a few percent increase in conductance when the frequency was increased from 2 to 50 kilocycles/second. The 50-kilocycles/second values are reported in the figure.

#### DISCUSSION OF THE CONDUCTIVITY OF SODIUM BENTONITE SUSPENSIONS

The weight conductance-concentration curves appear to have the same general shape as those reported by Tattje (1942) for sols of silver iodide. Tattje has interpreted these curves on the basis of experimental data for the transference numbers of the ions in the system that he obtained. The theoretical background of his explanation is Overbeek's (1941, 1943) theory of electrophoresis. Because of the analogy of Tattje's results on silver iodide with our results on sodium bentonite, it will be of interest to review Tattje's interpretation.

In very dilute sols of AgI, Tattje found that the weight conductance is inde-

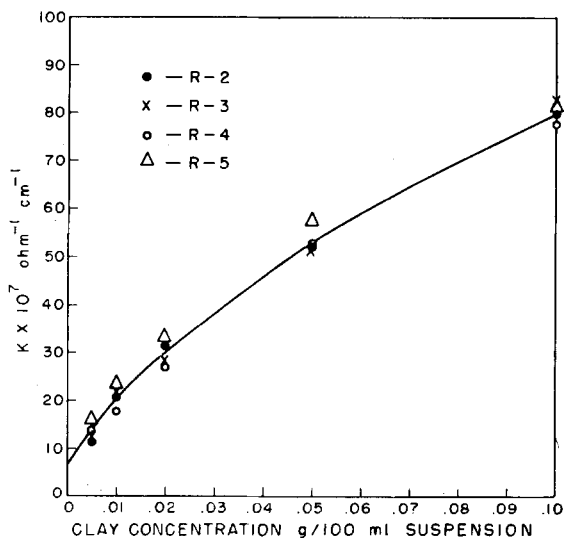


FIGURE 3.— Specific conductance of sodium bentonite suspensions at low clay concentrations for four particle-size fractions.

pendent of the AgI concentration. Remarkably enough, the magnitude of the weight conductance in this region shows that the AgI micelle is completely dissociated: The AgI particle transports its full negative charge electrophoretically and all the counter ions contribute to the conductance with their infinite dilution mobility.

With increasing sol concentration the weight conductance drops sharply. At the same time the transference data show that the mobility of the counter ions decreases sharply, whereas the electrophoretic mobility of the particles is not appreciably affected.

Overbeek explains the decrease of the counter-ion mobility as follows: With increasing sol concentration the electrical double layer becomes less expanded. Then there are two reasons why the counter-ion mobility decreases. One reason is that by friction the water immediately surrounding the moving particle moves with the particle; consequently the velocity of the counter ions close to the particle is reduced by the local fluid velocity. This effect is called "electrophoretic retardation." The more compressed the double layer is, the more important this effect will be. It appears that at sufficiently high sol concentrations, the counter ions even move in the same direction as the particles and obtain a negative mobility.

A second retarding effect on the counter ions is the result of a deformation of the double layer around the moving particle. The double layer is broken off in front of the particles and is restored behind it. A finite time of relaxation results in a dissymmetry of the double layer. This causes a reduction of the

electric field around the particle and a reduction of the velocity of the counter ions ("relaxation retardation").

Overbeek has given a quantitative treatment of these two retardation effects. The theory is valid for zeta potentials that are smaller than 25 millivolts. If the theory is nevertheless applied to higher zeta potentials the predicted effect of the retardations on the weight conductance of a silver iodide sol with Na ions as counter ions amounts to at most 30 to 40 percent. Tattje actually observed a larger effect, amounting to about 80 percent, which may be due to the limitations of the theory to low zeta potentials.

With a further increase of the concentration of the sol, the weight conductance and also the counter-ion mobility go through a minimum. The subsequent rise of the conductance and counter-ion mobility was explained by Tattje as a result of surface conductance taking over.

This point is of particular interest to us. Although Tattje did not elaborate on the mechanism, it may be inferred that one should visualize the occurrence of particle bridging between the electrodes at sufficiently high sol concentrations so that conductance can take place along a continuous surface. Such a bridging would immobilize the particles and thus eliminate the two retardation effects on the counter ions. Therefore, the counter-ion mobility and the conductance would increase. Obviously, this gain in conductance is reduced by the loss of the electrophoretic charge transport by the particles, but apparently the net effect on the conductance is an increase. With increasing sol concentration the immobilization of the particles becomes complete and a rigid gel is obtained. At this stage the conductance is determined solely by the mobility of the counter ions along the surface of the particles in the gel; in other words, by the surface conductance.

This concludes the observations on silver iodide. In the case of sodium bentonite an analogous explanation of the data may be taken as the basis for a quantitative discussion. We have not yet substantiated the analysis of our conductivity results by transference experiments as Tattje did. This was for the following reasons: It appeared that our curves are shifted, with respect to those for AgI, to a much smaller concentration range. This must be due to the plate-like shape of the clay particles which gives rise to particle interactions at much smaller weight concentrations than in the case of the more or less spherical AgI particles. Therefore the transference experiments on clay could best be done by tracer techniques, requiring a method of tagging the clay lattice. However, as we were primarily interested in the range of concentrations where the system is immobilized, we did not put much effort into the study of the dilute suspensions at this time.

Nevertheless, some quantitative information about the structure of the double layer may be obtained at very low sol concentrations, which will be of interest in discussions of the mechanism of the surface conductance of the gels. The question may be answered whether or not the clay micelle, like the AgI micelle, behaves as a fully dissociated micelle at very low sol concentration. In other

words, is the observed weight conductance at concentrations of 0.005 to 0.01 g/100 ml the sum of the contributions of all the counter ions and the fully ionized particle or is it less?

The magnitude of the weight conductance for a fully ionized sodium bentonite particle can be calculated as follows:

The double-layer charge of sodium bentonite is found from the base-exchange capacity and the surface area. The total surface area, including the interlayer areas, of one gram of sodium bentonite as computed from unit cell weight and dimensions is about 750 m<sup>2</sup>. The base-exchange capacity is 90 meq/100 g. Then the charge density on the surface is

$$\sigma = \frac{90 \times 6.02 \times 10^{20} \times 1.6 \times 10^{-19} \times 10^6}{750 \times 10^4 \times 100} = 11.6 \mu \text{ Coulomb/cm}^2$$

The specific conductance of the sol at a certain low concentration  $c$  in the case of complete dissociation is:

$$K_c = NQU + nqv \quad (3)$$

where:  $K_c$  is the specific conductance at concentration  $c$  (ohm<sup>-1</sup> cm<sup>-1</sup>)

$Q$  is the particle charge (Coulomb)

$U$  is the electrophoretic mobility of the particle (cm<sup>2</sup> sec<sup>-1</sup> volt<sup>-1</sup>)

$N$  is the number of particles per cm<sup>3</sup>

$q$  is the charge of the Na<sup>+</sup> cation (Coulomb)

$v$  is the mobility of the Na<sup>+</sup> cation (cm<sup>2</sup> sec<sup>-1</sup> volt<sup>-1</sup>) = 5 × 10<sup>-4</sup>

$n$  is the number of cations per cm<sup>3</sup>.

$$N = 0.01 \times c \times \frac{1}{b^2 dps},$$

where:  $c$  is the clay concentration (g per 100 ml suspension)

$b$  is the length of the side of a square clay plate (cm)

$d$  is the thickness of a unit layer of bentonite (cm)

$p$  is the number of unit layers per particle

$s$  is the density of the dry clay (g/cm<sup>3</sup>) = 2.70.

$Q$  is given by  $Q = 2\sigma b^2$

$nq = NQ$  because of the electroneutrality of the particle.

Then equation (3) becomes:

$$\frac{K_c}{c} = 0.02 \times \frac{\sigma}{dps} (U + v) \text{ ohm}^{-1} \text{ cm}^{-1}. \quad (4)$$

In this treatment it is assumed that the cations between the layers of the particles move with the particle as a whole and do not contribute to the conductance. If they were still able to move to some extent with respect to the particle the expected  $K_c/c$  value formulated above should be considered a minimum. The maximum value would be obtained if all interlayer cations had their infinite dilution mobility, which is equivalent to putting  $p = 1$  in equation (4).

According to particle-size determinations the most likely value for the degree of layer association is  $p = 2$ . The electrophoretic velocity of the particles as

determined by the microelectrophoretic method (Rutgers, Facq, and van der Minne, 1949) was  $3.0 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$ . Substituting these data in (4) gives  $K_c/c = 3500 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  as a minimum value, which is 2.5 times the measured value. The best explanation of the low value observed is that a considerable portion of the counter ions is immobilized by adsorption on the surface, or, in other words, that the particle is incompletely dissociated, contrary to AgI particles. It is hard to say whether the two retardation effects also contribute to the reduction in conductivity owing to a possible compression of the diffuse part of the double layer, even in these high dilutions, although this does not seem very likely.

An incomplete dissociation of the micelles is in qualitative agreement with previous conclusions about the double-layer structure of sodium bentonite: From the fact that unit layers of sodium bentonite associate in stacks of at least 2, even in dilute suspensions, it was inferred that the majority of the counter ions would be held in the Stern layer by specific adsorption forces (van Olphen, 1954).

A reduction of the weight conductance is observed on increasing the clay concentration. The reduction is of the same order of magnitude as observed by Tattje for AgI sols with Na as the counter ion. A factor of 2.35 (57 percent reduction) is found for the R-5 fraction and a factor of 3.1 (68 percent reduction) for the R-2 fraction. This may be the result of the two retardation effects although as in the case of AgI the effect is larger than would be expected from the theory.

When comparing the minimum values of the conductance with the theoretical value for complete dissociation and no retardation, the total reduction of the weight conductance amounts to a factor of 6 for the R-5 fraction (83 percent reduction) and a factor of 7.8 for the R-2 fraction (87 percent reduction). As such a large total reduction is probably far beyond the effect of the two retardation mechanisms, the concept of limited dissociation in extremely dilute suspensions as indicated above seems very likely.

It is supposed that the minimum is reached when particle interaction begins to lead to bridging between the electrodes and that beyond this point surface conductance gradually takes over. The minimum, which is reached at a concentration of 0.2–0.3 g/100 ml covers a smaller concentration range with smaller particle sizes. It has been shown (van Olphen, 1956) that the smaller the particle size, the lower the concentration at which gels develop; therefore, it is reasonable that the conductance begins to rise again at lower concentrations for smaller particle sizes than for larger particle sizes. The final values of the weight conductance for the concentrated gels are, however, the same for different particle size fractions. Apparently, it is immaterial whether the clay network is made of small or of large plates.

That particle interaction really begins to make itself felt at the concentration where the minimum in the weight conductance curve is reached could be cor-

robored by both viscosity and light transmission studies which will be discussed in a later section.

Our main problem now is to evaluate the surface conductance from the weight conductance of the highly concentrated gels. The reasoning applied is as follows:

The scaffolding structure of the gel is idealized as a cubic network of square clay plates. Every individual clay plate consists of a stack of  $p$  unit layers of bentonite and therefore has 2 external surfaces and  $2(p-1)$  internal surfaces. The total double-layer charge is supposed to be the same on all surfaces and is equal to  $11.6 \times 10^{-6}$  Coulomb/cm<sup>2</sup>. It is further assumed that the average mobility of all the counter ions on the external surfaces is a fraction  $a$  of their infinite dilution mobility, and that of the ions on the internal surfaces, a fraction  $b$ .

Consider a clay plate of 1 cm by 1 cm bridging between electrodes 1 cm apart. The expected  $K_c/c$  value calculated for this one bridge will be the same as for a number of parallel bridges, as both  $K_c$  and  $c$  will increase in the same proportion.

The weight of one plate is  $p/(\frac{1}{2}A)$ , where  $A$  is the total internal and external surface area of 1 g of sodium bentonite which is  $750 \times 10^4$  cm<sup>2</sup>. This plate is contained in the unit conductivity cell of 1 cm by 1 cm by 1 cm; therefore the concentration is  $c = 100p/(\frac{1}{2}A)$  g/100 ml suspension.

The plate links the electrodes with a number of parallel conducting surfaces: 2 sq cm of external surface and  $2(p-1)$  sq cm of internal surfaces. Therefore the total conductance is the sum of these specific surface conductances:

$$K_c = 2 K_s^e + 2(p-1) K_s^i.$$

It is assumed in this picture that the presence of any imperfect contacts between the particles that are due to their irregular shapes does not imply highly resistant barriers between the particles. As there is a diffuse ionic double layer on the particle edges, the assumption of sufficiently well-conducting local gaps between the particles seems warranted. If not, the following estimate of surface conductance should be considered a minimum estimate.

The specific surface conductance of the external surfaces is  $K_s^e = a\sigma v$  and that of the internal surfaces  $K_s^i = b\sigma v$  where  $\sigma$  is the charge density and  $v$  the infinite dilution mobility of the counter ion Na.

Therefore,

$$K_c = 2a\sigma v + 2(p-1)b\sigma v,$$

and the expected value of

$$K_c/c = [a/p + b(p-1)/p]0.01(\frac{1}{2}A)2\sigma v. \quad (5)$$

Substitution of the numerical values for  $\sigma$ ,  $A$ , and  $v$  ( $= 5 \times 10^{-4}$  cm<sup>2</sup> sec<sup>-1</sup> volt<sup>-1</sup>) results in

$$K_c/c = [a/p + b(p-1)/p]4350 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

However, in a cubic network only two-thirds of the plates are parallel to the field and contribute to the conductivity, whereas one-third, which are perpen-



dicular to the field, do not make any contribution. Therefore the expected value for

$$K_c/c = m \times 2900 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}, \quad (5a)$$

in which  $m = a/p + b(p-1)/p$ .

The specific surface conductance, on substitution of the numerical values for  $\sigma$  and  $v$ , becomes

$$K_s^e = a \times 5.8 \times 10^{-9} \text{ ohm}^{-1} \text{ and } K_s^i = b \times 5.8 \times 10^{-9} \text{ ohm}^{-1}. \quad (6, 6a)$$

From the experimental value of  $m$ , limiting values for  $a$  and  $b$  can be derived. As the double layer between the unit layers is more condensed than that on the external surfaces the value of  $a$  is probably larger than  $b$ . Then the following limits are obtained:

If  $pm$  is larger than 1,  $1 > a > m$  and  $m > b > (mp-1)/(p-1)$ .

If  $pm$  is smaller than 1,  $mp > a > m$  and  $m > b > 0$ .

The observed value for  $m = 1600/2900 = 0.55$ . As  $p$  is at least equal to 2, the wider limits for  $a$  and  $b$  are  $1 > a > 0.55$  and  $0.55 > b > 0.1$ , and the surface conductance is between 5.8 and  $3.2 \times 10^{-9} \text{ ohm}^{-1}$  for the external surfaces and between 3.2 and  $0.58 \times 10^{-9}$  for the internal surfaces. This is as close as one can get to the real values. For an analysis of the behavior of the formation resistivity factor it will be sufficient to consider the external and internal surfaces to be equivalent and to assign the average value of  $3.2 \times 10^{-9}$  to the surface conductance of the particle.

In view of the condensed character of the electrical double layer of sodium bentonite it is rather surprising that the Na ions still have such a relatively high mobility. Although it was concluded earlier that the sodium ions have an appreciable adsorption potential at the surface, indicating a high field strength close to the surface and perpendicular to it, these ions seemingly are able to move along the surface in the comparatively weak field of 0.03 volt/cm that was used in the measurements. However, as long as the mechanism of the mobility of ions in free solution is still not fully understood quantitatively, it would be premature to speculate on the mechanism of the mobility of adsorbed ions along a charged surface, where the structure of the liquid is certainly different from that in free solution.

Although the above data suggest that even the cations in the highly condensed double layer between the unit bentonite layers contribute to some extent to the conductivity (since  $m > 0.5$ ), they do not supply a definite conclusion regarding such a contribution or, in other words, the magnitude of the fractions  $a$  and  $b$ . It will be of interest, therefore, to study the conductance of suitable nonexpandable clays in order to obtain an idea of how large  $a$  can get.

It may be remarked that at the frequencies used, there might be an electroosmotic addition to the mobility of the counter ions, at least on the external surfaces. This would increase the expected  $K_c/c$  value and thus reduce the value of  $m$ .

On the other hand any tendency to randomization of the plate positions in the gel network would reduce the factor of two-thirds which is valid for the

cubic stacking, amounting to a smaller expected  $K_c/c$  value and thus an increase of the value of  $m$ .

Both effects were not accounted for in the above computation of the surface conductance but they may largely compensate each other.

### PARTICLE INTERACTION FROM VISCOSITY AND LIGHT TRANSMISSION

The leveling off in the weight conductance–clay concentration curves at 0.15 to 0.3 percent clay was considered a result of the beginning of particle interaction, leading to occasional immobilization of the particles. Some additional support for this assumption was obtained from viscosity and light transmission measurements at different clay concentrations.

#### *Viscosity*

At low suspension concentrations the specific viscosity ( $\eta_{sp} = \eta_{rel} - 1$ ) is proportional to the total volume fraction  $\phi_c$  of the suspended material, independently of particle size and shape. The proportionality factor, however, is a function of particle shape. For large thin discs, considered as ellipsoids of revolution, this relation is, according to Peterlin (Philippoff, 1942, p. 17),

$$\eta_{sp} = \frac{4}{3\pi} q\phi_c \text{ where } \phi_c = 0.01 c/\rho,$$

in which  $q$  is the ratio between major and minor axis of the ellipsoid and  $\rho$  the density of the hydrated clay particle.

Therefore  $\eta_{sp}/c$  should be a constant as long as there is no particle interaction and in this region the asymmetry of the particles is found from  $q=235\rho(\eta_{sp}/c)$ . As soon as particle interaction occurs,  $\eta_{sp}/c$  must increase.

In Figure 4,  $\eta_{sp}/c$  is plotted versus the clay concentration for the various particle-size fractions. From the horizontal part of the curves at low concentration the asymmetry  $q$  is calculated and tabulated in the figure, showing an increase with decreasing particle size.

It is seen from the figure that the rise of  $\eta_{sp}/c$  sets in at a concentration of 0.15 percent for the smallest fractions R-5 and R-4, at 0.25 percent for R-3, and at 0.3 percent for R-2. This is in good agreement with the inference from the conductance data.

#### *Light Absorption Measurements*

The optical density of the suspensions was measured with a Beckman spectrophotometer at various wave lengths. Results for the fractions R-2 to R-5 are given in Figure 5 for a wave length of 4000Å.

At low concentrations the optical density increases proportionally to the clay concentration. Apparently Beer's law is followed in this region. In order to show the effect of wave length, the slopes of the optical density–clay concentration curves at low concentrations are collected in Table 1.

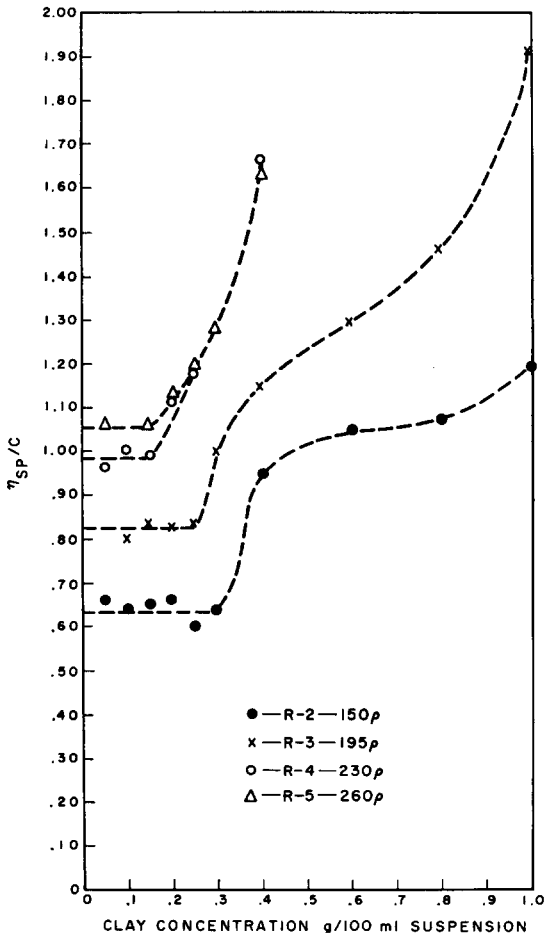


FIGURE 4.— $\eta_{sp}/c$  as a function of clay concentration—for five size fractions of sodium Wyoming bentonite.

At higher concentration the optical density increases less rapidly with the concentration. This can be interpreted as a result of the decline in the increase of the scattering intensity with concentration. The reason for this is an interference of the light scattered by interdependent particles, and therefore the change in slope of the optical density curve is an indication of particle interaction. This occurs at clay concentrations between 0.15 percent and 0.25 percent, which is in good agreement with the conclusion from conductivity and viscosity data.

In closing it may be remarked that it is not so surprising that particle interaction in clay suspensions becomes apparent at such low concentrations, if we

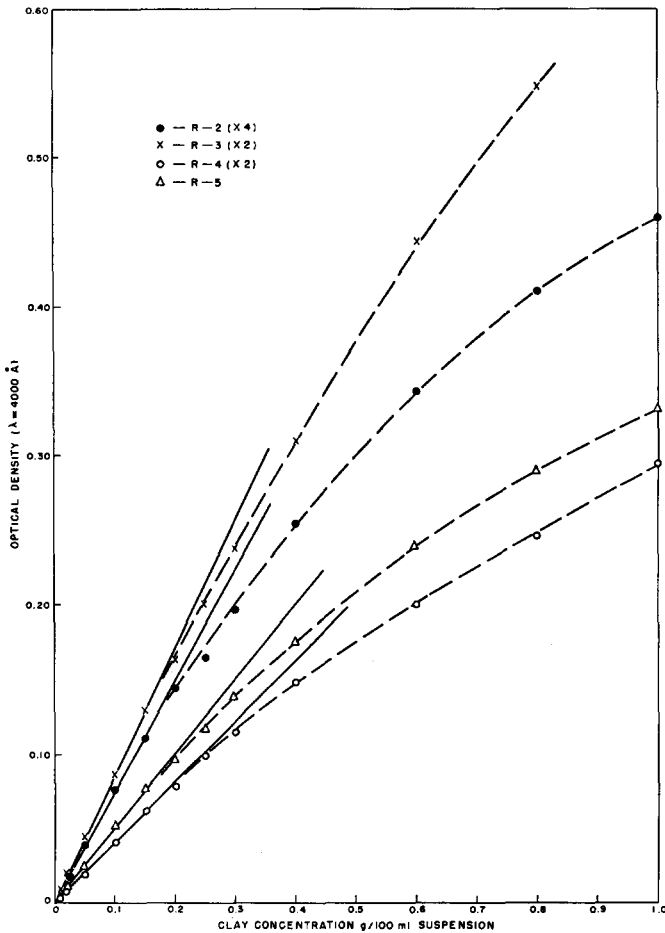


FIGURE 5.—Optical density at  $\lambda \approx 4000\text{A}$  of Na bentonite suspensions as a function of clay concentration for four size fractions.

TABLE 1.—OPTICAL DENSITY:  $d/c$  VALUES FOR FOUR Na BENTONITE FRACTIONS AT FOUR WAVE LENGTHS

Fraction	Wave Length			
	3200 A	4000 A	4800 A	5600 A
R-2	4.8	3.0	2.1	1.6
R-3	3.22	1.70	1.07	0.81
R-4	1.95	0.80	0.48	0.31
R-5	1.66	0.50	0.20	0.14

$d$  = optical density  
 $c$  = clay concentration in g/100 ml

keep in mind that the particles are large thin plates. The following little computation is quite illustrative: If all the particles contained in 100 ml of a 0.01 percent clay suspension of particle size 8500A by 8500A and 2 unit layers thick were lined up, a ribbon would be obtained which would easily reach clear across the state of Texas.

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