DIELECTRIC PROPERTIES AND HIGH FREQUENCY CONDUCTANCE OF WYOMING BENTONITE

Thesis for the Degree of Ph. D.

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Wilfred L. Polzer

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This is to certify that the

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Dielectric Properties and High Frequency Conductance of Wyoming Bentonite

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Wilfred L. Bolger

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Max M. Mortland
Major professor

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By

Wilfred L. Polzer

A THESIS

Submitted to the School for Advanced Graduate Studies
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ABSTRACT

The purpose of this research was to study the dielectric behavior and high frequency conductance of Wyoming bentonite clay and to study the effect of the type of exchangeable cation on these electrical properties of the bentonite clay.

Eight different kinds of base saturated clays of seven different concentrations were studied in this experiment. The cations associated with the bentonite clays were aluminum, barium, calcium, magnesium, lithium, sodium and potassium. Electrolyte solutions of sodium, potassium and calcium chloride were also used as a means of comparing the results obtained from the clay suspensions. The range in frequency at which the measurements were made varied from one kilocycle per second to 192 megacycles per second. A General Radio Type 650-A impedance bridge was used to measure the capacitance of the clay suspensions in the kilocycle frequency range. A high frequency oscillator was used to show the effect of frequency on the capacitance and the conductance of clay suspensions in the megacycle frequency range. All the results were interpreted on the basis of a parallel equivalent circuit in order to account for the effect of the measuring cell on the electrochemical results obtained.

The results obtained showed that both the capacitance and the conductance are dependent on the frequency at which the measurements are made. The capacitance of the clay suspensions was found to decrease with an increase in frequency. When based on the specific

conductance of the clay suspensions the capacitance was found to vary with the kind of cation associated with the clay in the low megacycle frequency range. The order of difference was Li clay > Na clay > K clay.

The high frequency conductance of the clay suspensions was greater than the high frequency conductance of electrolyte solutions at similar specific conductances. A difference in high frequency conductance was also obtained between the various kinds of base saturated clays. The order of response was as follows:

Ba clay > Ca clay > Mg clay > Li clay > Na clay > K clay.

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CHAPTER I

INTRODUCTION

All materials are generally classified into three main divisions; conductors, semi-conductors and non-conductors, which are based upon the conductivity or resistivity of the material. The divisions may overlap each other since the resistivities for these divisions are only arbitrary. The semi- and non-conducting materials are considered dielectrics which are characterized by a dielectric constant. However, all materials have dielectric properties even though they may be conductors.

If an alternating voltage is applied across a material, whether it is a solid, liquid or gas, a current results depending upon the electrical properties of the material. The current which arises from the applied voltage may be derived from one or both of two types of electrochemical behavior. One type of electrochemical behavior results in electrical energy being converted into heat energy. This conversion is due primarily to migration of ions through a voltage gradient. The other type of electrochemical behavior results from a displacement of charge which also takes place under the influence of a voltage gradient. However, no energy is converted to heat because a restoring mechanism is also present so that the energy which is used to displace the charge on one part of the alternating cycle is returned on the next part of the cycle. This current determines the capacitance of the material which, in turn, is a measure of the dielectric properties of the material.

The amount of current which arises from the applied voltage is dependent on the frequency of the alternating voltage. When the dielectric behavior of a colloidal suspension is measured at high frequencies, factors other than dielectric constants of components of the colloidal suspension have far more influence which results in an increased "apparent dielectric."

Curtis and Fricke (1937) measured the "apparent dielectric constants" of suspensions, including kaolin, in a frequency range from 0.25 to 2000 kilocycles per second. The values obtained reached as high as 40,000 at the low frequencies, but decreased rapidly as the frequency increased. These workers (1935) also measured electrical conductance up to 16,000 kilocycles per second of colloidal suspensions and found an increase in conductance with an increase in frequency.

Smyth (1955) with reference to dielectric constants, and Overbeek (1952) with reference to both dielectric constants and conductance, reported the results of various workers, showing that over certain ranges of frequency the dielectric constants of colloidal solutions are much larger than that of water, but that these values decrease with an increase in frequency. The large dielectric constants of colloidal solutions were attributed by Overbeek (1952) to either a permanent dipole moment or to the electric double layer of the colloids, more probably the latter. A rise in conductance was found to result with an increase in frequency. This was attributed to the oscillating movement of the particles being so rapid that the asymmetry of the double layer did not have time to develop to its full extent.

Soil scientists have been interested in capacitance measurements from a practical as well as from a theoretical point of view in the field of soil water. Edlefsen (1933) and Aleksandrov (1934), as reported by Thorne and Russell (1947), found an almost linear relationship between capacitance and soil moisture in the dry range of soil moisture up to moisture equivalent. Fletcher (1939) also found that soil colloids had an effect on the capacitance. Anderson and Edlefsen (1942) using Bouyoucous blocks, but measuring capacitance instead of resistance, found very large values between the moisture equivalent and the permanent wilting point. Using the theory of Fricke and Curtis (1937), Anderson (1942) based the high range of values on polarization at the interfaces of a dielectric dispersed in water. Thorne and Russell (1947) concluded that their results of capacitance measurements could be qualitatively based on the fact that there is a high degree of orientation of the dipolar water molecules at the solid-liquid interfaces within the system.

The purpose of this research was to study the dielectric behavior and high frequency conductance of Wyoming bentonite clay and to study the effect of the type of exchangeable cation on these electical properties of the bentonite clay.

CHAPTER II

SAMPLE PREPARATION

The Wyoming bentonite used in this experiment included seven concentrations of eight different cation-saturated clays. The concentrations ranged from 0.00176 to 0.04526 grams of clay per milliliter of suspension. The cations used for clay saturation included sodium, potassium, lithium, magnesium, calcium, barium, aluminum and hydrogen.

The clay was put into suspension with a Waring blend mixer. The suspension was diluted to approximately one percent clay and allowed to settle over night at which time the < 2 micron clay particles were separated. The <2 micron clay suspension was then passed through a column of Amberlite Resin IR-4B in order to exchange any anions present in the clay suspension. The clay was then tested for chloride and sulfate ions. Sulfuric acid was added to a small portion of clay, the clay flocculated and then the supernatant solution tested for chlorides. If no white precipitate formed from the addition of silver nitrate the clay was considered free of chlorides. Conversely, hydrochloric acid was used to replace any sulfate ions from the clay and calcium nitrate was used as the testing reagent for sulfates in the supernatant solution.

The clay was then electrodialyzed to approximately pH 5.5. It was felt that this pH value was high enough so that the hydrogen ions would not cause lattice decomposition of the clays, yet low enough so that the cation exchange resin would be more efficient in replacing the cations associated with the clay with the desirable kind of cations.

The cation exchange capacity of the bentonite was determined by hydrogen saturating a sample of clay with Amberlite Resin IR-120. The sample was immediately titrated with a standard sodium hydroxide. The exchange capacity was determined both potentiometrically and conductiometrically as shown in Figure 1.

The clay used for sodium saturation was passed through hydrogen saturated Amberlite Resin IR-120 and the proper amount of sodium hydroxide (87.6 milliequivalents per 100 grams of clay) was added to neutralize the clay.

The lithium and potassium saturated clays were prepared by passing the anion free clay suspensions through a column of lithium and potassium saturated Amberlite Resin IR-120, respectively, instead of hydrogen saturating the clay first.

The calcium saturated clay was prepared by taking anion free clay and saturating it with tenth normal calcium chloride. The ratio of added calcium chloride to the number of exchange sites on the clay was approximately fifty to one. The chlorides were washed free with the use of suction. Silver nitrate was used to test for chlorides. The aluminum saturated clay was prepared in the same manner as the calcium saturated clay. In addition, the pH of the suspension was kept below neutral in order to keep the aluminum chloride from precipitating on the clay.

Similarly the barium and magnesium saturated clays[1] were prepared from clays that had been removed of free anions and hydrogen saturated. Barium chloride and magnesium oxide were used to saturate the clays with barium and magnesium, respectively. The barium saturated clay was then washed free of chlorides.

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[1]The barium and magnesium saturated clays had been prepared by Dr. H. Jacobs for use in his Ph. D. Thesis work.

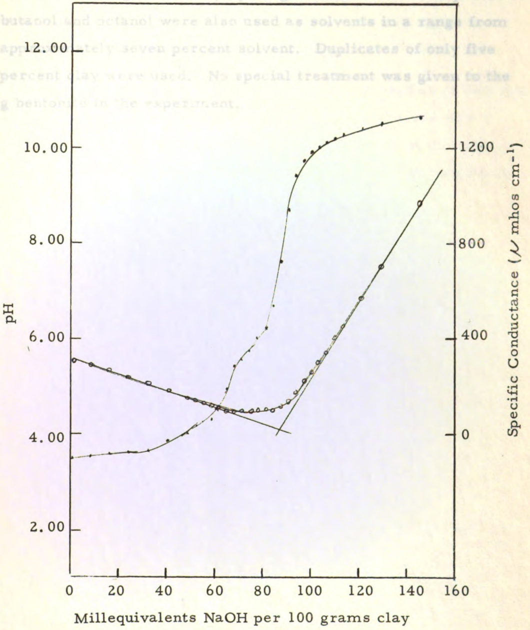

Figure 1. Titration curves to determine the cation exchange capacity of Wyoming bentonite clay.

Duplicate samples of quartz sand-Wyoming bentonite mixtures were prepared for determining high frequency response to moisture in the range from one-third to fifteen atmospheres of pressure. Samples of five, ten and fifteen percent clay by weight were used in this problem. Water, butanol and octanol were also used as solvents in a range from zero to approximately seven percent solvent. Duplicates of only five and ten percent clay were used. No special treatment was given to the Wyoming bentonite in the experiment.

CHAPTER III

DIELECTRIC PROPERTIES

Experimental Apparatus

The method used to determine the dielectric properties of bentonite was that of measuring the capacitance of the clay suspensions with a General Radio type 650-A impedance bridge. A diagram of the capacitance comparison circuit of this bridge is found in Figure 2. The condition of balance for the bridge is that

$$Z_1 Z_X = Z_2 Z_3 \tag{1}$$

where Z_1, Z_2, Z_3 and Z_X are the complex impedances of the four arms.

Since the impedances of the four arms are complex, two requirements must be met in balancing the bridge. One requirement is that the magnitudes of the impedances must satisfy equation (1). Secondly, the sum of the phase angles of one pair of opposite arms must equal the sum of the angles of the other opposite arms.

If the impedance values of the bridge circuit in Figure 2 are substituted into the impedance values in equation (1) where

$$Z_1 = R_1 \quad ; \quad Z_2 = R_3 \qquad \text{(2) and (3)}$$

$$Z_3 = R_3 - j\,\frac{1}{\omega\, C_3} \tag{4}$$

$$Z_X = R_X - j\,\frac{1}{\omega\, C_X} \tag{5}$$

then

$$R_1(R_X - j\,\frac{1}{\omega\, C_X}) = R_2(R_3 - j\,\frac{1}{\omega\, C_3}) \tag{6}$$

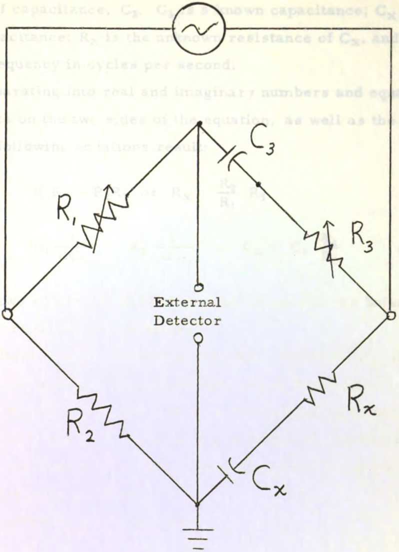

Figure 2. Capacitance comparison bridge circuit diagram; R_1 - CRL rheostat, R_2 - known resistance, R_3 - D rheostat, C_3 - known capacitance, R_X- unknown resistance, C_X- unknown capacitance.

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where R_1 and R_2 are known resistors; R_3 is a known resistor plus the resistance of capacitance, C_3; C_3 is a known capacitance; C_x is an unknown capacitance; R_x is the unknown resistance of C_x, and ω is 2π times the frequency in cycles per second.

By separating into real and imaginary numbers and equalizing the real parts on the two sides of the equation, as well as the imaginary terms, the following equations result:

$$R_1 R_x = R_2 R_3 \quad \text{or} \quad R_x = \frac{R_2}{R_1} R_3 \tag{7}$$

$$R_1 \frac{1}{\omega C_x} = R_2 \frac{1}{\omega C_3} \quad \text{or} \quad C_x = C_3 \frac{R_1}{R_2} \tag{8}$$

From these two equations, it is shown that there are two balance conditions which requires two variables.

C_x is determined by adjusting the CRL rheostat, R_1, the values being calibrated in capacitance readings. R_x is determined by adjusting R_3. The R_3 values are calibrated in the dissipating factor, D, which is defined as $R\omega C$ where R is the total resistance of arm three at a frequency of one kilocycle, ω is 2π times frequency in cycles and C is the capacitance of arm three.

If ω is assumed to be one, then

$$D = RC \quad \text{or} \quad R = \frac{D}{C} \tag{9}$$

If R_x and R_3 of equation (7) are substituted for R in equation (9), then

$$R_x = \frac{D_x}{C_x} = \frac{R_2}{R_1} \cdot R_3 = \frac{R_2}{R_1} \frac{D_3}{C_3} \tag{10}$$

$$D_x = \frac{R_2}{R_1} D_3 \frac{C_x}{C_3} \tag{11}$$

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C_x is then substituted by equation (8)

$$D_x = \frac{R_2}{R_1} D_3 \frac{C_3}{C_3} \frac{R_1}{R_2} \tag{12}$$

or

$$D_x = D_3$$

therefore

$$D_3 = R_x C_x \tag{13}$$

R_x can then be calculated from equation (13).

An oscilloscope, Model 130A, made by the Hewlett-Packard Company at Palo Alto, California, was used to determine the balance point. A sensitivity of 0.05 volts per centimeter was used throughout the experiment for the oscilloscope. An audio oscillator Model 200CD also made by the Hewlett-Packard Company was used as the external frequency generator with an output voltage of 90 volts.

The capacitance cell was made up to two 12 inch x 16 inch and two 12 inch x 18 inch copper sheets, and one 1 3/4 inch x 2 1/4 inch brass plate. The four copper sheets were connected in series with one another, while the brass plate was connected in parallel with the copper sheets. Cardboard, impregnated with a mixture of beeswax and paraffin was used as insulation between the copper sheets. Boards, 3/4 inch thick, were bolted on the outside of the copper sheets to keep the distance between the sheets constant. A mixture of beeswax and paraffin was applied to the edges of the cell in order to keep the humidity between the sheets as constant as possible. A diagram of the cell is shown in Figure 3. The distance of 1 1/4 inches between the brass plate and the copper sheet was kept constant with the use of plastic material. The plastic also served as a container for the material to be measured. The brass plate was covered with a thin film of beeswax-paraffin mixture

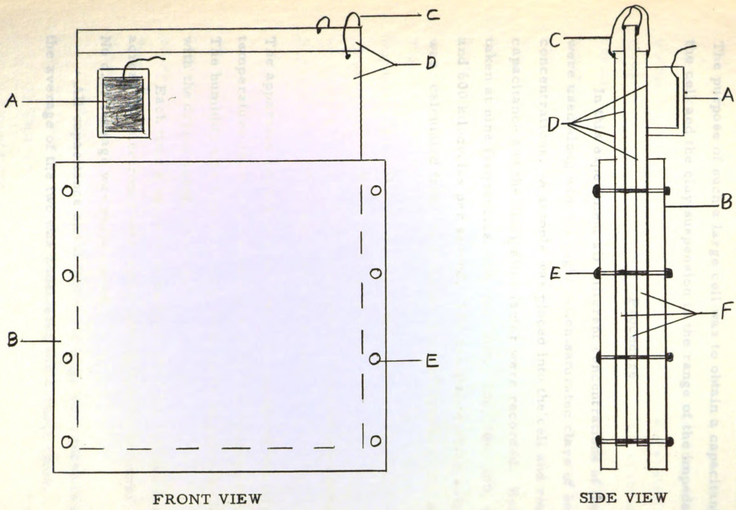

Figure 3. Diagram of the capacitance cell; A - cell container with brass electrode, B - 3/4 inch thick wooden boards, C - wire connecting copper sheets, D - copper sheets, E - bolts connecting wooden boards, F - cardboard impregnated with a mixture of beeswax and paraffin.

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in order to prevent passage of direct current between the electrodes. The purpose of such a large cell was to obtain a capacitance for both the cell and the clay suspension in the range of the impedance bridge.

Procedure

In this experiment six different concentrations of NaCl and $CaCl_2$ were used along with the eight cation-saturated clays of seven different concentrations. A sample was placed into the cell and readings of both capacitance and the dissipation factor were recorded. Readings were taken at nine frequencies; one, ten, fifty, 100, 200, 300, 400, 500, and 600 kilocycles per second. The resistance of the suspensions was calculated from the D factor through equation; $D = R \omega C$ where

D = dissipation factor

R = resistance in ohms

$\omega = 2 \pi$ time frequency in cycles per second

C = capacitance in farads.

The apparatus and the suspensions to be measured were kept in a constant temperature room at a temperature of 25 ± 0.5 degrees centigrade. The humidity was kept in a range from 50 to 65 percent relative humidity with the drying agent, silica gel.

Each time a suspension was placed in the cell the d.c. leakage across the electrodes was tested with a Triplett ohmmeter Model 630-A. No d.c. leakage was encountered.

All capacitance and D factor readings were taken in duplicate and the average of the two was considered the correct value.

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Results

The results for the capacitance measurements are given in Tables II and III. Figures 4 and 5 show the dependence of capacitance change on the specific conductance of the clay suspension at eight different frequencies. In Figures 36, 37, 38 and 39, of the appendix, the deviation of measurements from the drawn curves given in Figure 5 is presented. Curves showing the dependence of capacitance change on concentration of clay suspension are found in Figures 6, 7 and 8. The change in capacitance is based on the capacitance of the pure solvent, water. Instead of absolute capacitance the change in capacitance was used in order to explain the results on a theoretical basis.

Greater deviation occurred at the higher frequencies employed. This was attributed to error in obtaining the true null point on the impedance bridge. The null point was increasingly more difficult to obtain as high frequencies were used because of the limitations of the oscilloscope. Another source of error could have been due to a fluctuation of humidity. The relative humidity could only be kept within a range of 50 to 65 percent.

The capacitances of sodium chloride and calcium chloride solutions were also measured. There was essentially no difference in the capacitance change of the electrolyte solutions and those of the clay suspensions at similar specific conductances. Since the conductance of these electrolyte solutions was not in the lower range of conductance of the clay suspension the results were not plotted.

The following relationship were observed from the data in Figures 4, 5, 6, 7 and 8.

1) Capacitance is dependent on the frequency at which the measurements are made.

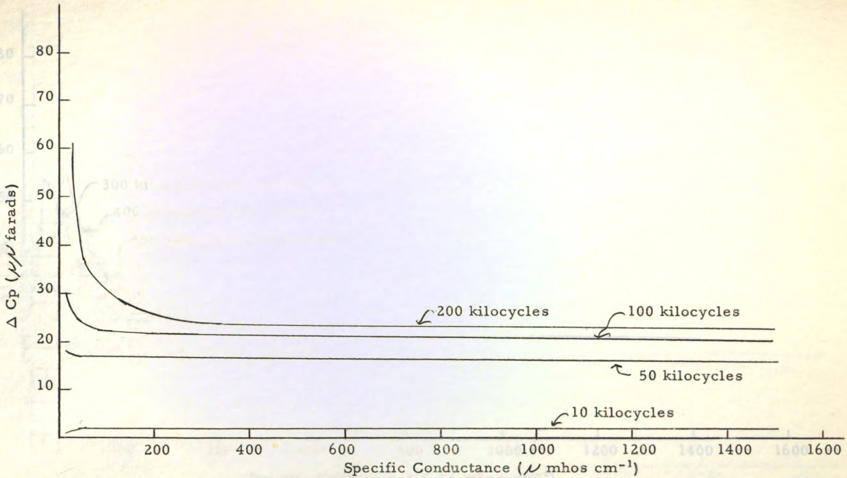

Figure 4. The relationship of the change in parallel capacitance to the specific conductance of the clay suspensions at 10, 50, 100 and 200 kilocycles per second.

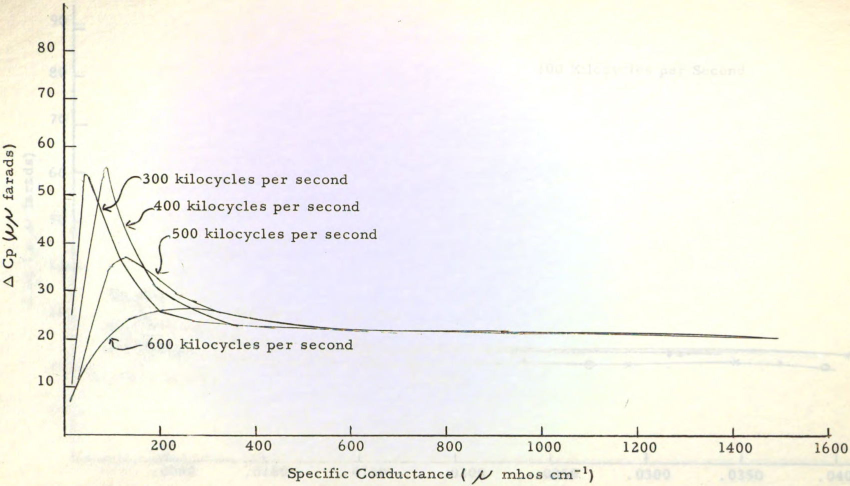

Figure 5. The relationship of the change in parallel capacitance to the specific conductance of the clay suspensions at 300, 400, 500 and 600 kilocycles per second.

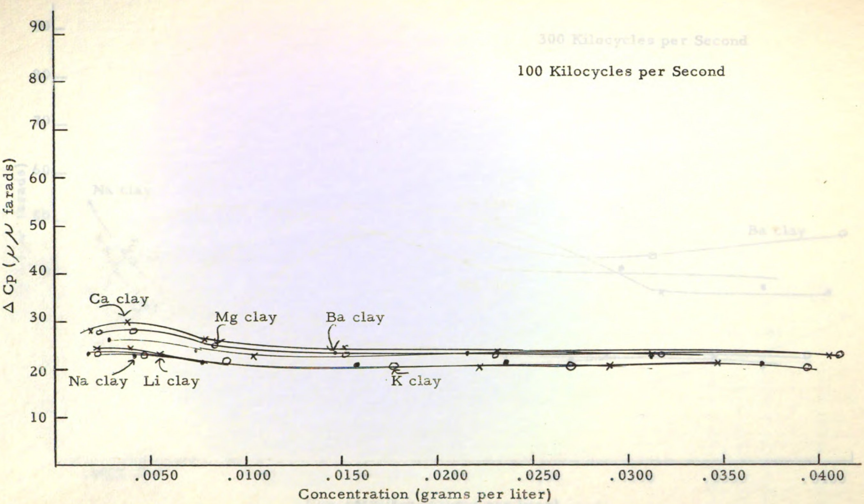

Figure 6. The relationship of the change in parallel capacitance to the concentration of the clay suspensions at 100 kilocycles per second.

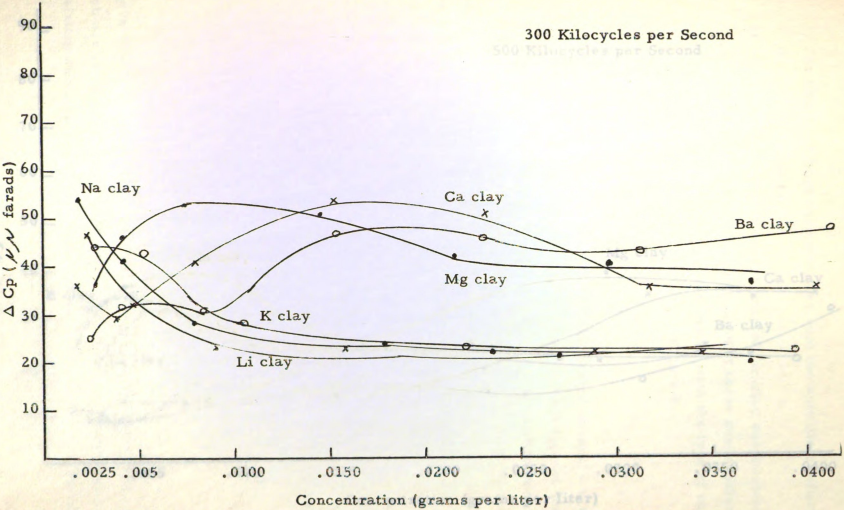

Figure 7. The relationship of the change in parallel capacitance to the concentration of the clay suspensions at 300 kilocycles per second.

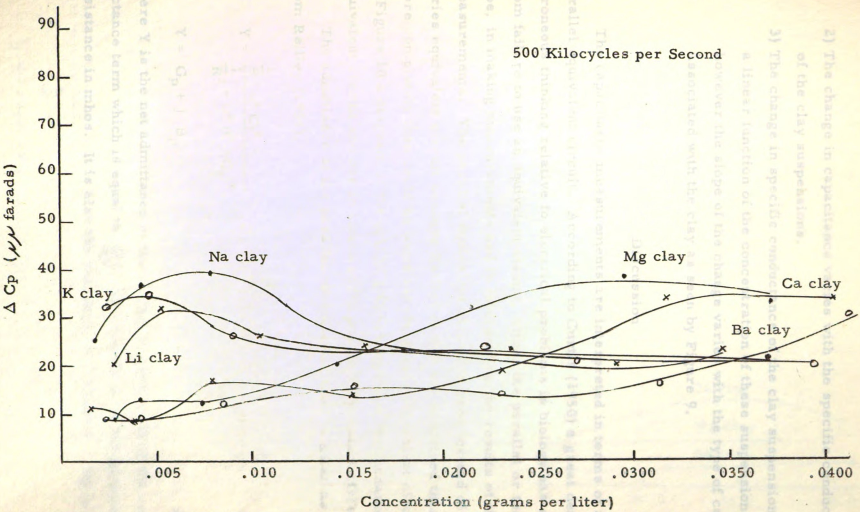

Figure 8. The relationship of the change in parallel capacitance to the concentration of the clay suspensions at 500 kilocycles per second.

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2) The change in capacitance varies with the specific conductance of the clay suspensions.

3) The change in specific conductance of the clay suspensions is a linear function of the concentration of these suspensions, however the slope of the change varies with the type of cation associated with the clay as seen by Figure 9.

Discussion

The capacitance measurements are interpreted in terms of a parallel equivalent circuit. According to Curtis (1950) a great deal of erroneous thinking relative to electrical problems in biology has resulted from failure to use an equivalent circuit, either the parallel or the series type, in making measurements and in interpreting the results of these measurements. The parallel equivalent circuit is used instead of the series equivalent circuit because Reilley (1954) has described this type more completely than could be found for the series equivalent circuit. In Figure 10 a diagram of the cell is given in terms of the fundamental equivalent circuit and one in terms of the parallel equivalent circuit.

The admittance of the parallel equivalent circuit is given as taken from Reilley (1954).

$$Y = \frac{\frac{1}{R} \quad \omega^2 C_1^2}{\frac{1}{R^2} + \omega^2 (C_1+C_2)^2} + j \frac{\frac{\omega C_1}{R^2} + \omega^3 (C_1C_1^2+C_2C_1^2)}{\frac{1}{R^2} + \omega^2 (C_1+C_2)^2} \tag{1}$$

$$Y = G_p + j \ B_p \tag{2}$$

where Y is the net admittance of the circuit in mhos. Gp is the conductance term which is equal to $\frac{1}{Rp}$, the reciprocal of the parallel resistance in mhos. It is also the real part of admittance. Bp is the

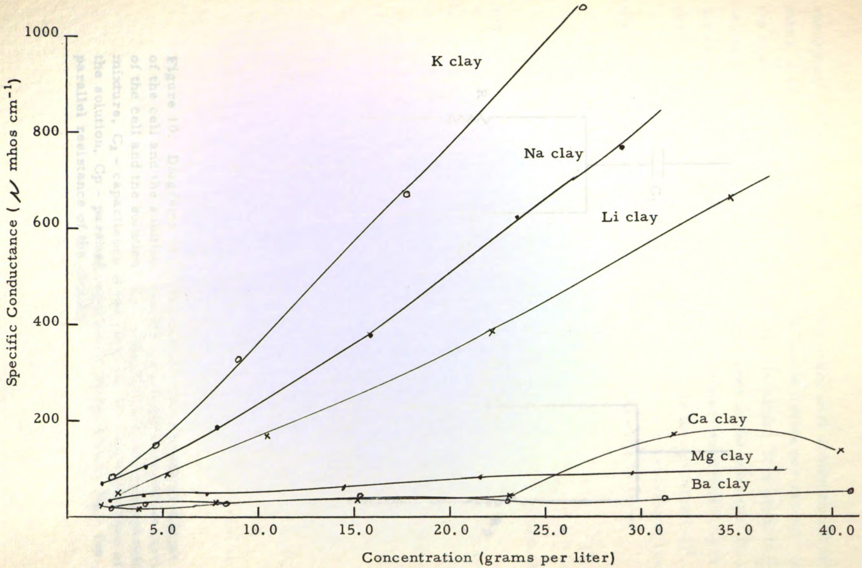


Figure 9. The relationship of specific conductance on the concentration of the clay suspensions.

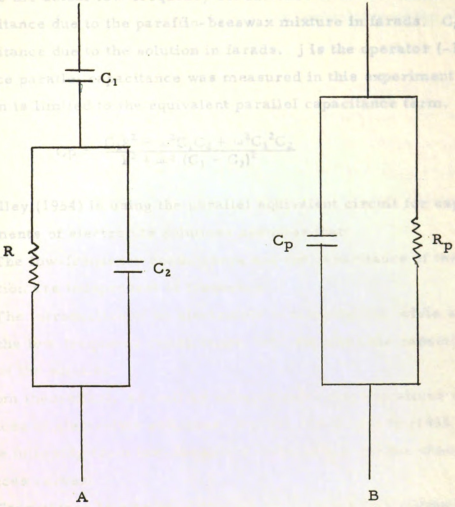


Figure 10. Diagrams of (A) the fundamental equivalent circuit of the cell and the solution, and (B) the parallel equivalent circuit of the cell and the solution; C_1 - capacitance of beeswax-paraffin mixture, C_2 - capacitance of the solution, R - the resistance of the solution, Cp - parallel capacitance of the circuit, R_p - the parallel resistance of the circuit.

susceptance term (ω Cp) which is the imaginary part of admittance in mhos. ω is equal to $2 \pi f$. f is the frequency in cycles per second. R is the actual resistance offered by the solution in ohms. R is equal to $\frac{1}{k}$ where k is the actual low-frequency conductance of the solution. C_1 is the capacitance due to the paraffin-beeswax mixture in farads. C_2 is the capacitance due to the solution in farads. j is the operator $(-1)^{\frac{1}{2}}$.

Since parallel capacitance was measured in this experiment the discussion is limited to the equivalent parallel capacitance term.

$$Cp = \frac{C_1k^2 + \omega^2C_1C_2 + \omega^2C_1{}^2C_2}{k^2 + \omega^2 (C_1 + C_2)^2} \qquad (3)$$

Reilley (1954) in using the parallel equivalent circuit for capacitance measurements of electrolyte solutions assumes that:

1) The low-frequency conductance and the capacitance of the solution are independent of frequency.
2) The introduction of an electrolyte to the solution, while altering the low-frequency conductance, will not alter the capacitance of the solution.

From theoretical, as well as experimental determinations of capacitances of electrolyte solutions, Reilley and McCurdy (1953) concluded the following from low-frequency conductance versus changes in capacitances curves:

1) Capacitance is a unique function of low-frequency conductance.
2) The response curves do not go through a maximum.
3) As the capacitance of the solution increases, the parallel capacitance decreases. This is shown by

$$\Delta \, Cp = \frac{C_1{}^2}{C_1 + C_2} \qquad (4)$$

which can be derived from equation (3) where Δ Cp is the difference in the extreme values of capacitance.

4) The k value at the mid-point where the capacitance is half way between its extreme values is dependent upon frequency, capacitance of the cell walls and the capacitance of the solution.

$$k \text{ mid-point} = \omega (C_1 + C_2) \quad (5)$$

In plotting the same type curve as Reilley and McCurdy (1953) did, but using clay suspensions instead of electrolyte solutions, the results are the same with one exception, a maximum is found whereas none occurred in the electrolyte solutions. This exception can be explained on the basis that capacitance is not independent of the low-frequency conductance. According to Reilley (1954) there is conflict as to the degree of dependence of capacitance on the conductance of electrolyte solutions and even the direction of this effect. However, Reilley (1954) found that most workers agree that successive small additions of electrolyte to the solvent cause the dielectric constant to decrease to a minimum and then rise and even surpass the value given for the pure solvent. Therefore, it seems logical that capacitance may be dependent on the conductance of clay suspensions.

A discussion of the factors affecting the dielectric constant of colloidal systems may be in order at this point. Overbeek (1952) considered four factors as affecting the dielectric constant of colloidal materials:

1) The volume effect would lower the dielectric constant, if sol particles, having a lower dielectric constant than that of the medium, are added to the medium.
2) The sol particles may possess a permanent dipole moment. This dipole moment is oriented by the electric field thereby enhancing polarization, thus causing an increase in the dielectric constant.
3) The electric double layer of the colloids may influence the dielectric constant. The particles may acquire a dipole moment when the outside electric field distorts the centers of gravity of the positive and negative charges, thus enhancing the dielectric constant.
4) The hydration or solvation may influence the dielectric constant. The water of hydration is under the influence of strong adsorption forces; thus the polarization may either be increased or decreased.

The sharp decrease in the capacitance of the clay suspension could possibly be attributed to an ion-dipole interaction of water and the "free" cations associated with the clay, which would decrease the polarization of water. This explanation was given for a decrease in capacitance of dilute electrolyte solution by Reilley (1954). Also, the solvation of water around the clay particles could give the same effect in dilute suspensions.

As the concentration of the clay particles increases, the conductance of the suspension also increases, but the concentration increases to a greater extent, because the dissociation of cations decreases with concentration as reported by Marshall (1949). Therefore as the concentration of the clay is increased the effect of the permanent dipole and that of the electric double layer could play dominant roles in changing the capacitance of the clay suspension. These factors would then be the reasons for the increase in the capacitance of the bentonite.

Once the conductance of the suspension reaches a certain point the concentration of the clay particles is so great that complete polarization of the suspension is not possible. This would mean that the resistance to movement of particles in the direction of the alternating electric field does not allow complete orientation or displacement of the charges responsible for polarization. Thus, any change in capacitance would decrease and even level off to an approximately constant value.

It is assumed in this discussion that a greater quantity of divalent cation-saturated clay is required to give the same capacitance effect as that of monovalent cation-saturated clay. The proportion of the divalent cation clays to monovalent cation clays needed to give this same effect is not known.

CHAPTER IV

HIGH FREQUENCY CONDUCTANCE

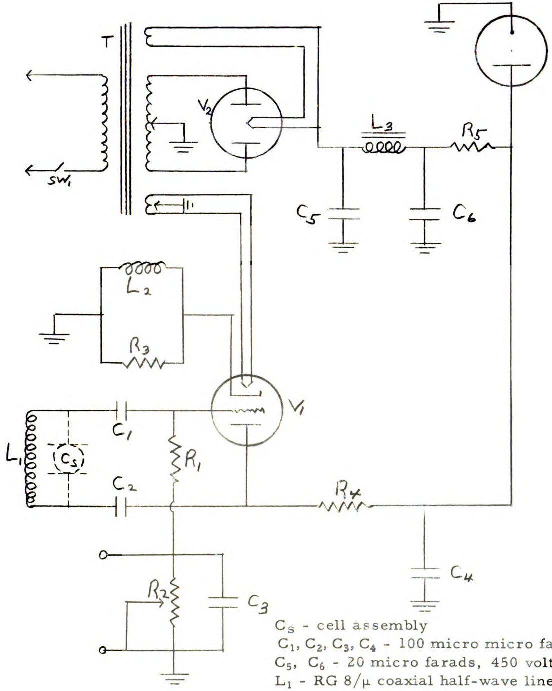
Experimental Apparatus

The high frequency conductance of the clay suspensions was determined with a high frequency titrimeter based on the apparatus designed by Johnson and Timnick (1956). The response may be measured by means of oscillator frequency change, grid current or voltage change, and plate current or voltage change. A schematic diagram of the circuit of the apparatus is given in Figure 11.

An a. c. current is passed through transformer T, and the rectified current is made more constant by the filter capacitances, C_5 and C_6, and the filter choke, L_3. The voltage is regulated by resistor R_5, and by V_3, a voltage regulator electron tube. The regulated d. c. voltage is then applied to V_1, an electron tube which is an oscillation generator.

The oscillation of the vacuum tube oscillator is based on feedback. Feedback means that part of the output voltage is fed back into the input voltage so that oscillation is independent of any external input voltage other than the initial input. Electrons are emitted from the cathode by the heating element of the tube. Since there is a potential difference between the cathode and plate, the electrons move toward the plate. The amount of electrons moving towards the plate is regulated by the bias, L_2 and R_3 in parallel. As the electrons move from the cathode to the plate, they pass through the grid.

Figure 11. Schematic diagram of high frequency conductance apparatus.



C_s - cell assembly
C_1, C_2, C_3, C_4 - 100 micro micro farads, mica
C_5, C_6 - 20 micro farads, 450 volts
L_1 - RG 8/μ coaxial half-wave line and coils
L_2 - 10 turns No. 22 wire wound around R_3
L_3 - filter choke, Gracoil 200925
R_1, R_4 - 15000 ohms, 1 - watt
R_2 - 1000 ohms, 1 - watt
R_3 - 100 ohms, 2 watts
R_5 - 5000 ohms, 10 watts
SW_1 - SPST toggle switch
T - transformer; 350-0-350, 70 milliamperes;
5 volts, 3 amperes; 6.3 volts, 3 amperes
V_1 - 955
V_2 - 5 3GT
V_3 - V R 150/30

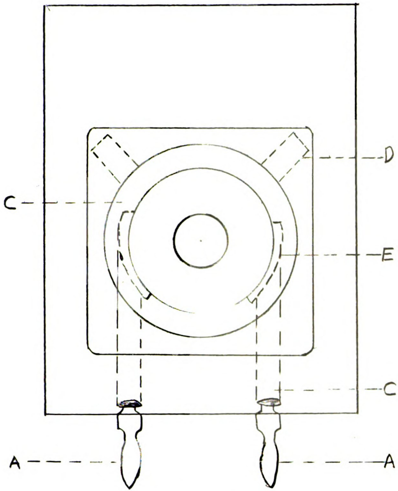
The oscillator is self-starting with the use of the grid-leak resistors, R_1 and R_2, and the capacitance C_1. At the instant power is applied, the absence of fixed bias permits the grid to draw a small amount of current which is required to charge the capacitor, C_S, and to begin the oscillation process. Once oscillation starts it is sustained by the output voltage on the load, R_4. The output voltage is largely controlled by the bias which adjusts itself by the charge on C_1.

As the amplitude of oscillation tends to decrease, the bias also drops causing the gain of the tube to rise, thus increasing the amplitude again. Meanwhile a part of the output voltage is fed back to the input through C_2 which makes up for the energy losses in the oscillating circuit.

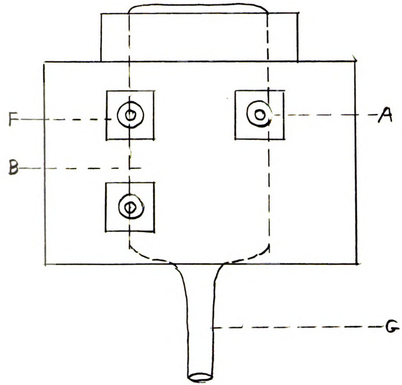
The change of composition of the unknown solution within the cell designated by C_s in the circuit will cause a change of the oscillating circuit load on the tube, V_1. This change has an effect on the oscillating frequency, grid current or voltage, and plate current or voltage. In this apparatus the change of grid voltage across R_2 with the change in the composition of the unknown solution was measured with a student potentiometer made by the Leeds and Northrup Company.

The inductance L_1, may be varied by changing the coil, which in turn changes the frequency at which the circuit oscillates. Thus the effect of frequency on the response to solutions can be measured. Six different plug in type coils, corresponding to frequencies ranging from 13 to 192 megacycles per second, were used in this experiment.

Diagrams of the cell used in this experiment are found in Figures 12 and 13. The glass container was enclosed in an aluminum box with a copper ring at the top in order to obtain proper shielding. The glass was supported in the box with plastic in order to make the cell more rigid. An outlet at the bottom of the cell allowed drainage of the clay



TOP VIEW



END VIEW

Figure 12. Schematic diagrams of the cell assembly of the high frequency conductance apparatus; A - banana jacks, B - glass container, C - shielding, D - plastic support, E - electrode, F - plastic wall, G - glass opening.

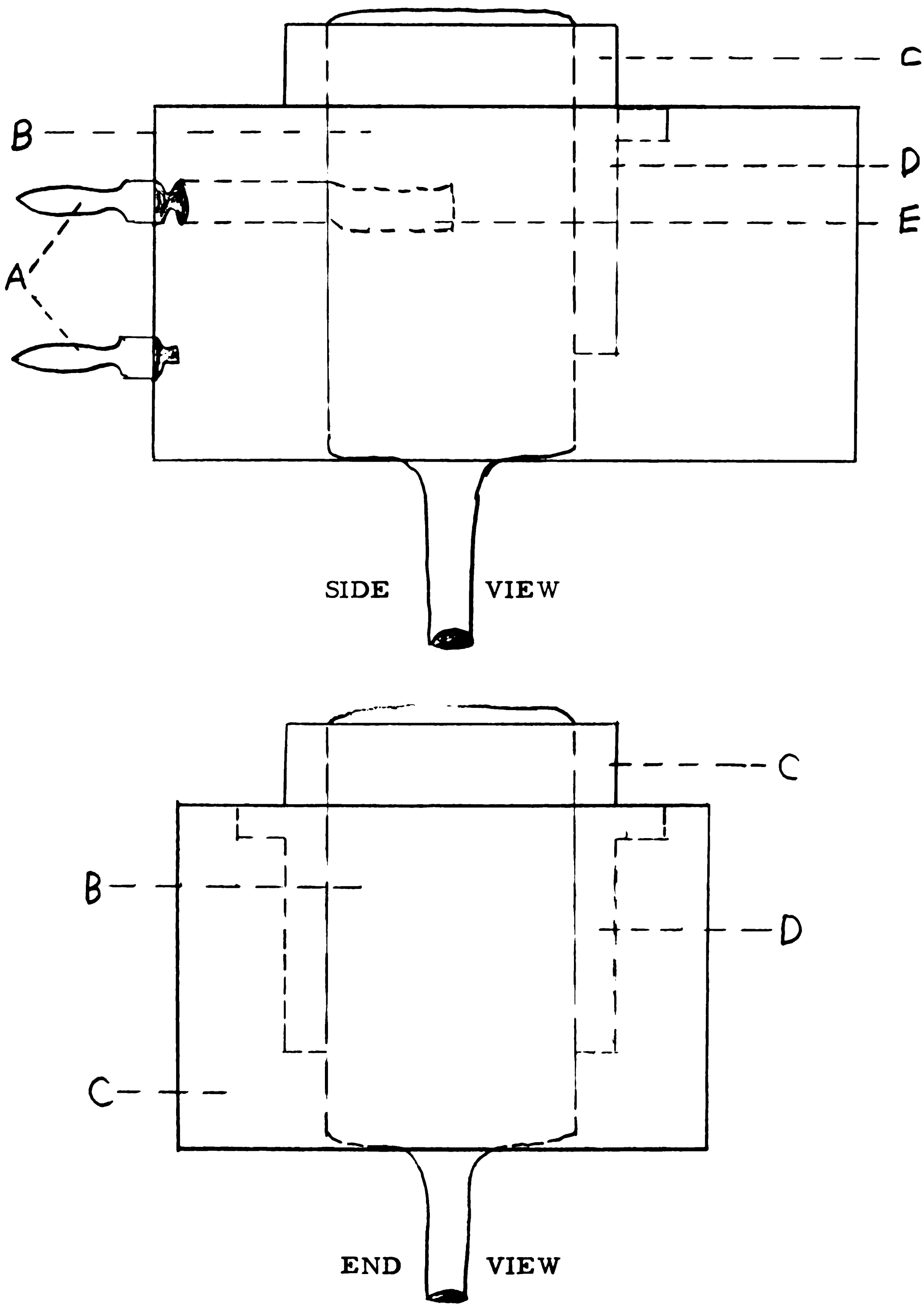


Figure 13. Schematic diagrams of the cell assembly of the high frequency conductance apparatus; A - banana jacks, B - glass container, C - shielding, D - plastic support, E - electrode.

suspensions without hindering the reproducibility of the cell. The cell box was bolted into place to allow more rigidity when measurements were taken.

Procedure

Thirteen different concentrations, 0.01 to 1.00 normal, of sodium chloride and potassium chloride were used to show the response of the high frequency oscillator to the conductance of strong electrolytes. Also, eight concentrations of sodium clay, ranging from 0.0116 grams to 0.1344 grams per milliliter were used to compare the response of bentonite to that of strong electrolyte solutions. Response was measured at six frequencies; 13, 30, 44, 57, 79 and 192 megacycles per second. The R_2 resistor of the oscillator was set at 936 ohms for each response.

The student potentiometer was standardized with a Weston cell before each series of measurements. The results were based on the difference in response with suspensions in the cell and with conductivity water in the cell.

In another part of the high frequency conductance experiment the response to sodium chloride and calcium chloride was recorded in addition to the response to the seven concentrations of eight different cation-saturated clays used in the capacitance measurements. In this case only four frequencies; 13, 44, 79 and 192 megacycles per second were used. The R_2 resistor was set at 1000 ohms. A different glass container was used in this series of measurements. All readings were taken in a constant temperature chamber at 25 $\pm$ 0.5 degrees centigrade.

An experiment was also set up using percent moisture and percent clay as variables in quartz sand-Wyoming bentonite clay mixtures. High frequency response was measured at all six frequencies.

Three levels of clay, 5, 10 and 15 percent, were studied. The moisture content was varied in part of the experiment by using the pressure plate and the membrane methods. The atmospheric pressure ranged from 1/3 atmosphere to 15 atmospheres. A lower range of moisture was obtained by adding water to the mixtures in small amounts, then allowing them to equilibrate for seven days. The percent moisture was determined by oven drying a small portion of the sample. Butanol and octanol were also used as solvents in this range of liquid variation. Only 5 and 10 percent clay mixtures were used for the lower range of moisture and alcohols.

Results

The results for high frequency conductance are given in three parts. In the first part the results show the effect of electrolyte solutions on high frequency response as compared to results obtained by Reilley and McCurdy (1953). The results also show the effect of sodium saturated Wyoming bentonite on high frequency response. The data are presented in Figures 14 through 22 and are expressed as negative deflection in volts. The negative deflections in volts represent an increase in the deflections of high frequency conductance. This can be explained on the basis of Ohm's Law. Voltage is directly related to resistance, but resistance is inversely related to conductance; therefore voltage is inversely related to conductance. If a decrease in voltage is obtained, an increase in conductance would be observed.

The pure solvent, water, represents zero deflection. Deflection was used because the absolute voltage could not be reproduced, due mainly to voltage fluctuations. In attempting to standardize the voltage with a Weston cell the galvanometer showed a very slow but continuous change in voltage with time.

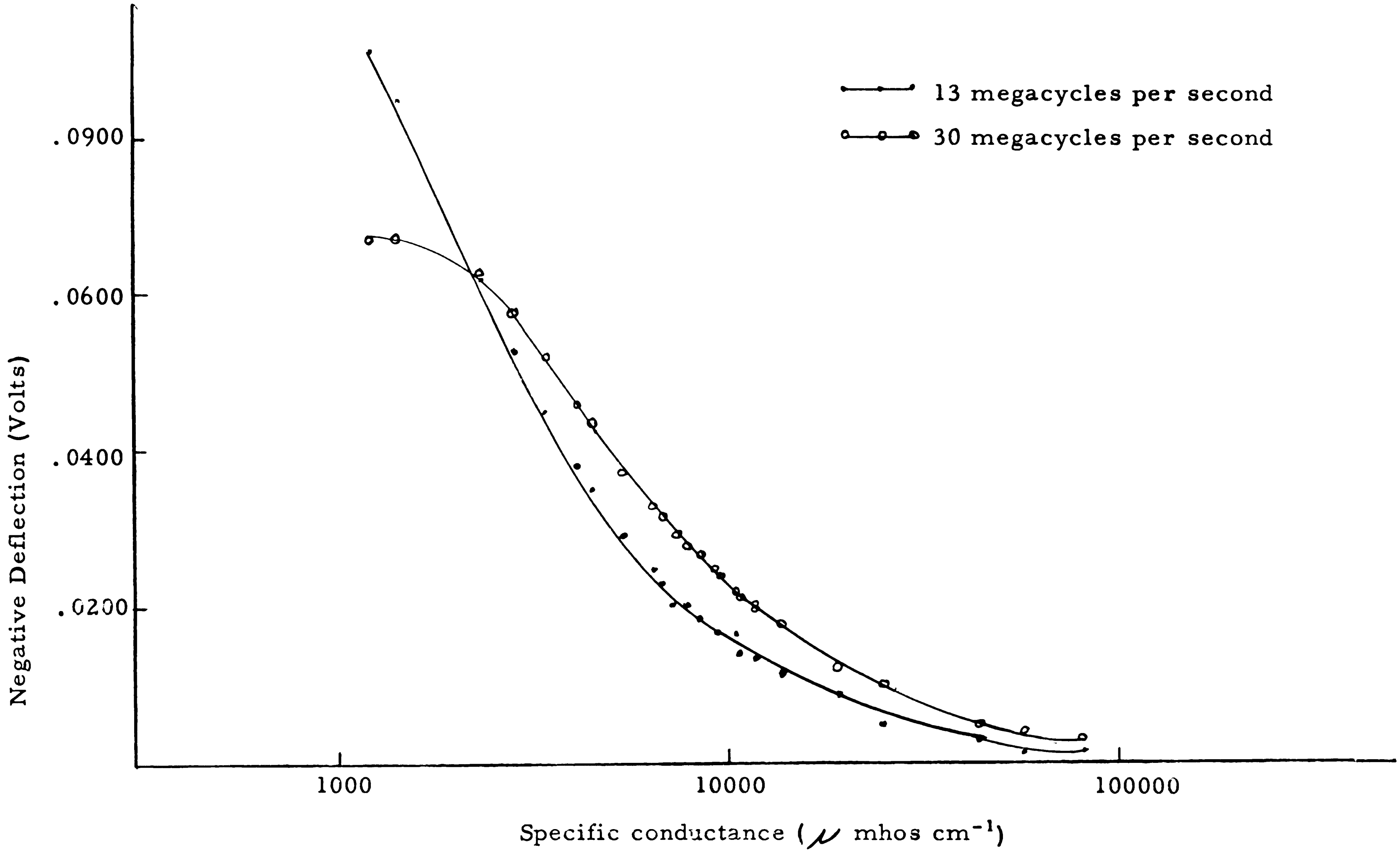


Figure 14. The relationship of high frequency response to the specific conductance of sodium chloride and potassium chloride solutions at thirteen and thirty megacycles per second.

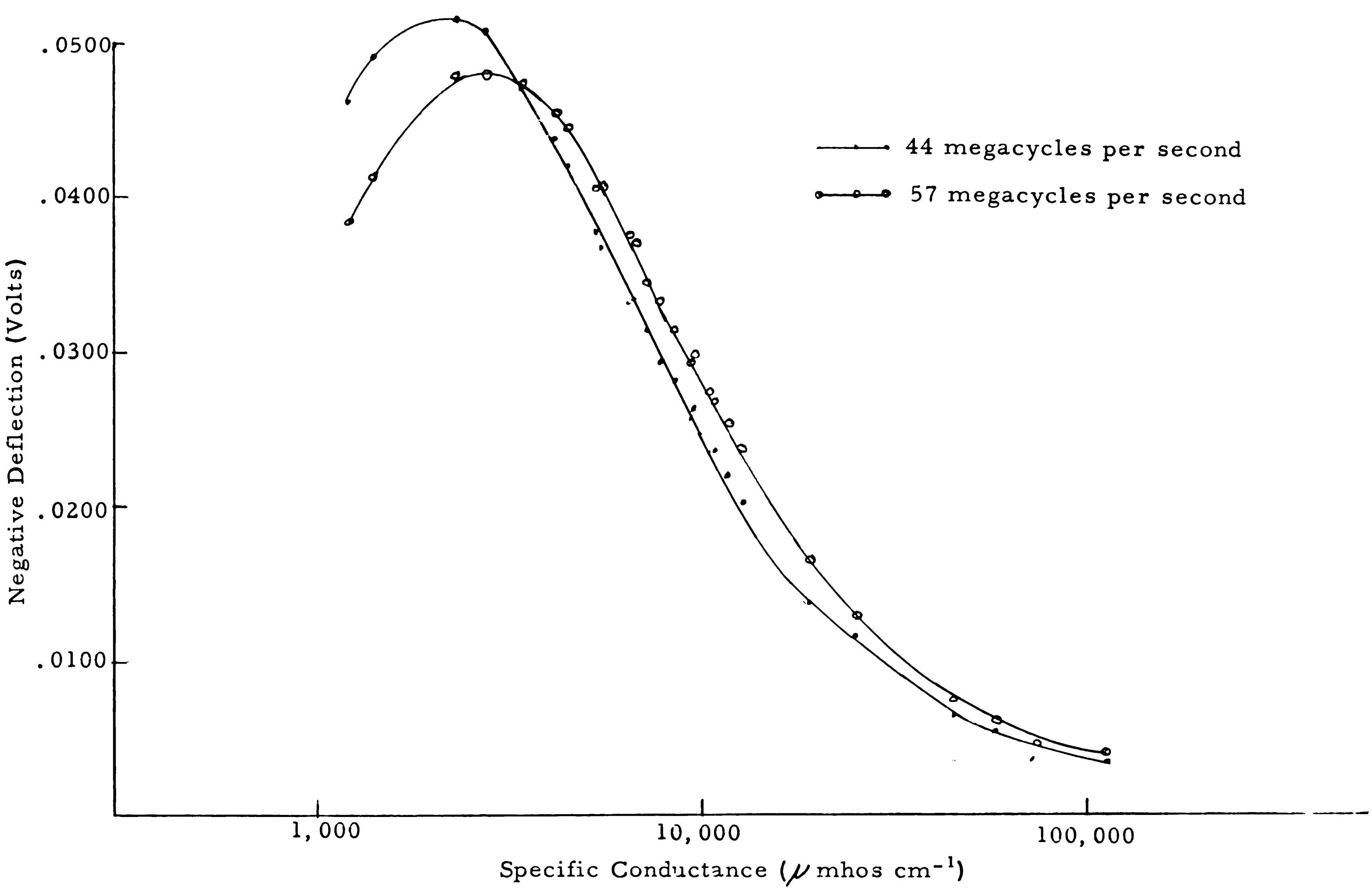


Figure 15. The relationship of high frequency response to the specific conductance of sodium chloride and potassium chloride solutions at forty-four and fifty-seven megacycles per second.

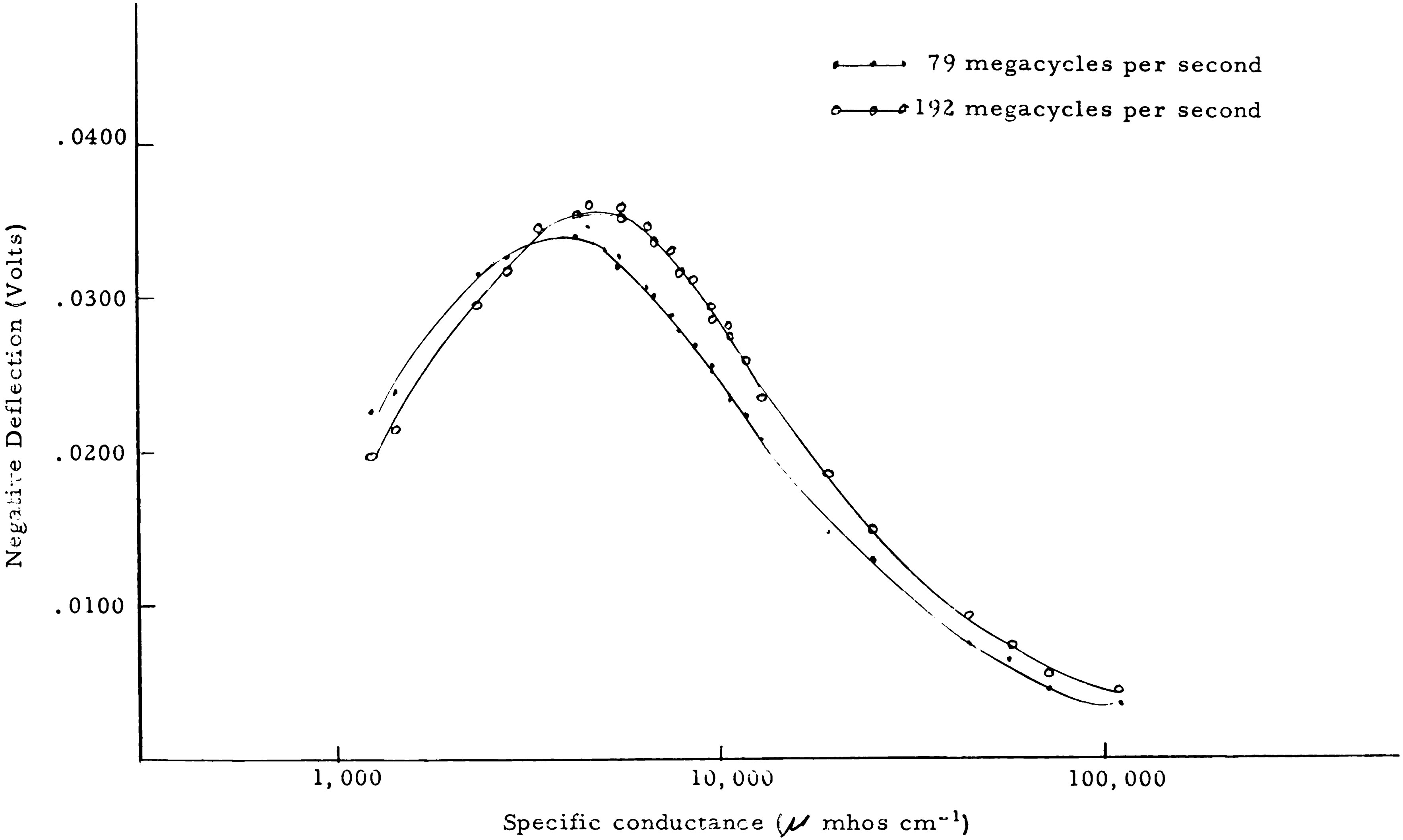


Figure 16. The relationship of high frequency response to the specific conductance of sodium chloride and potassium chloride solutions at seventy-nine and one hundred ninety-two megacycles per second.

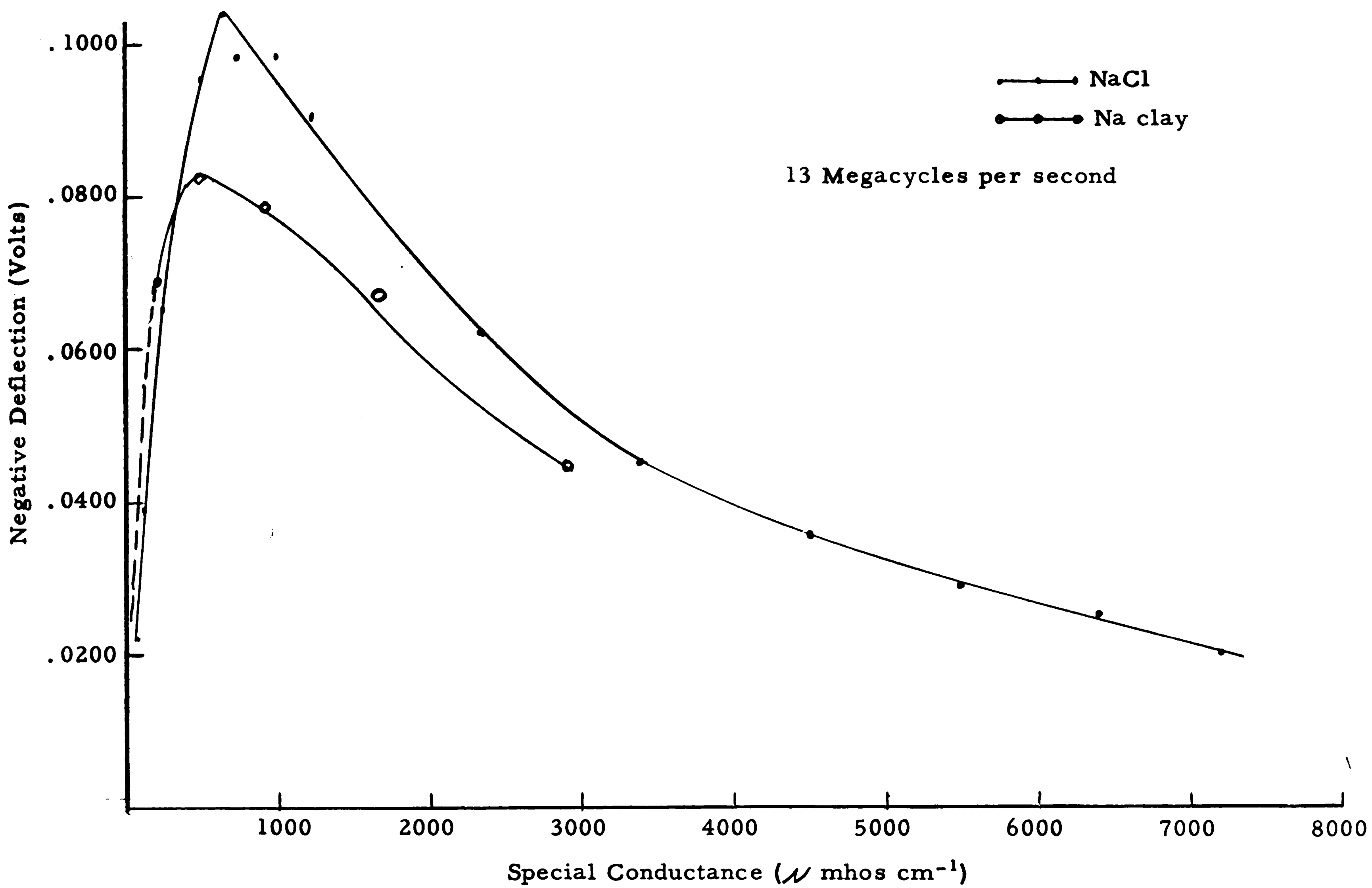


Figure 17. The relationship of high frequency response to the specific conductance of Na clay suspensions and sodium chloride solutions at thirteen megacycles per second.

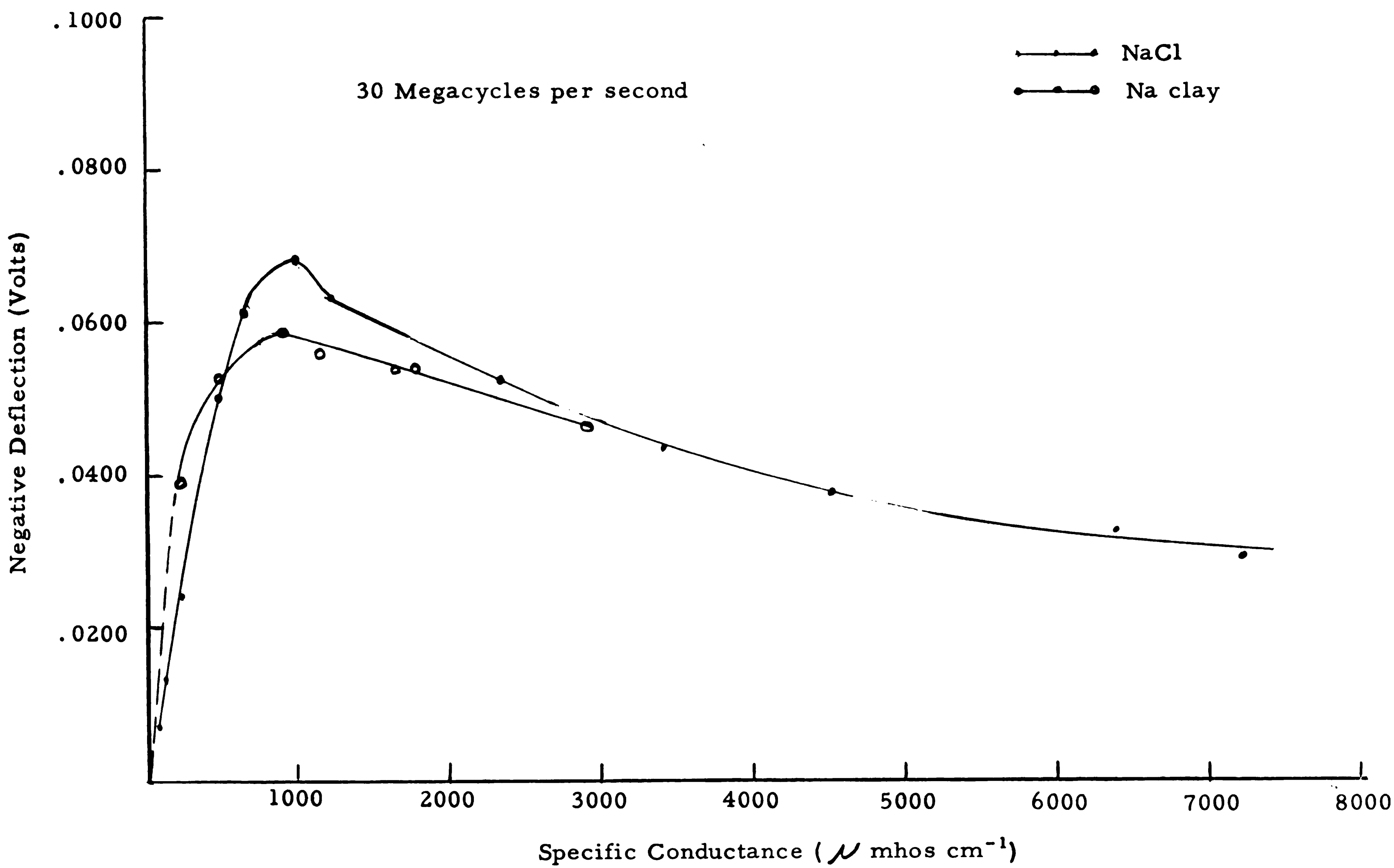


Figure 18. The relationship of high frequency response to the specific conductance of Na clay suspensions and sodium chloride solutions at thirty megacycles per second.

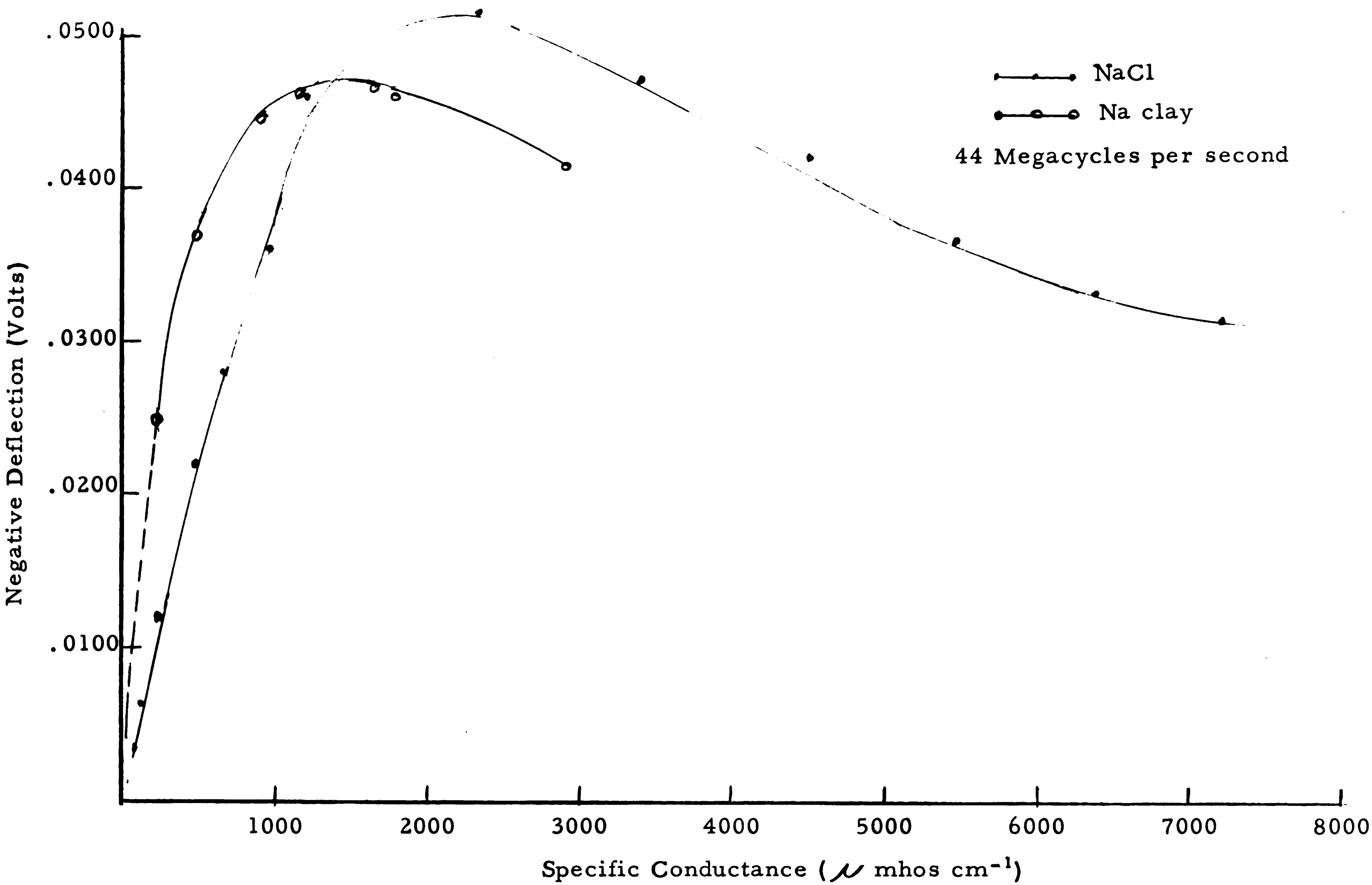


Figure 19. The relationship of high frequency response to the specific conductance of Na clay suspensions and sodium chloride solutions at forty-four megacycles per second.

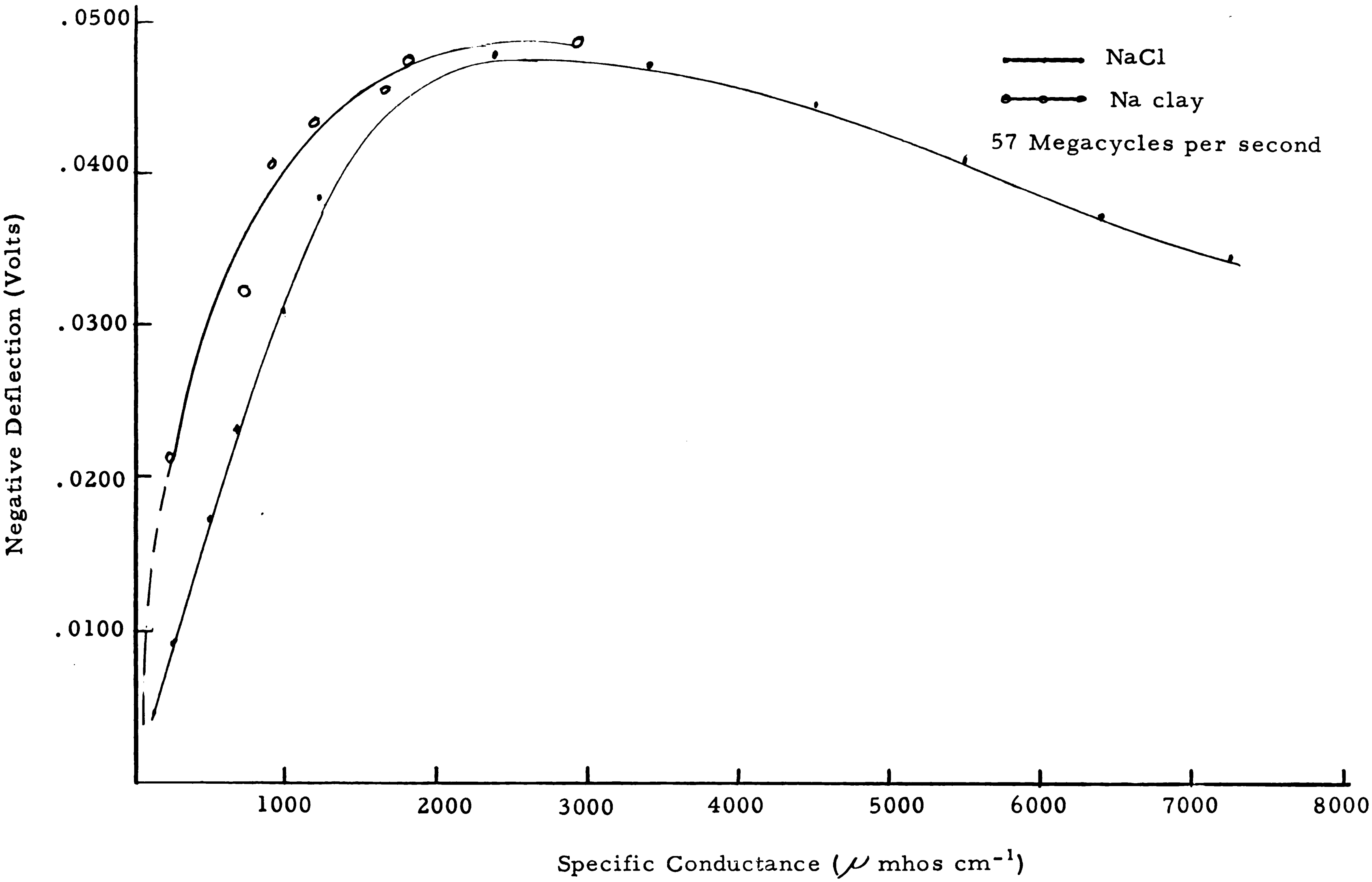


Figure 20. The relationship of high frequency response to the specific conductance of Na clay suspensions and sodium chloride solutions at fifty-seven megacycles per second.

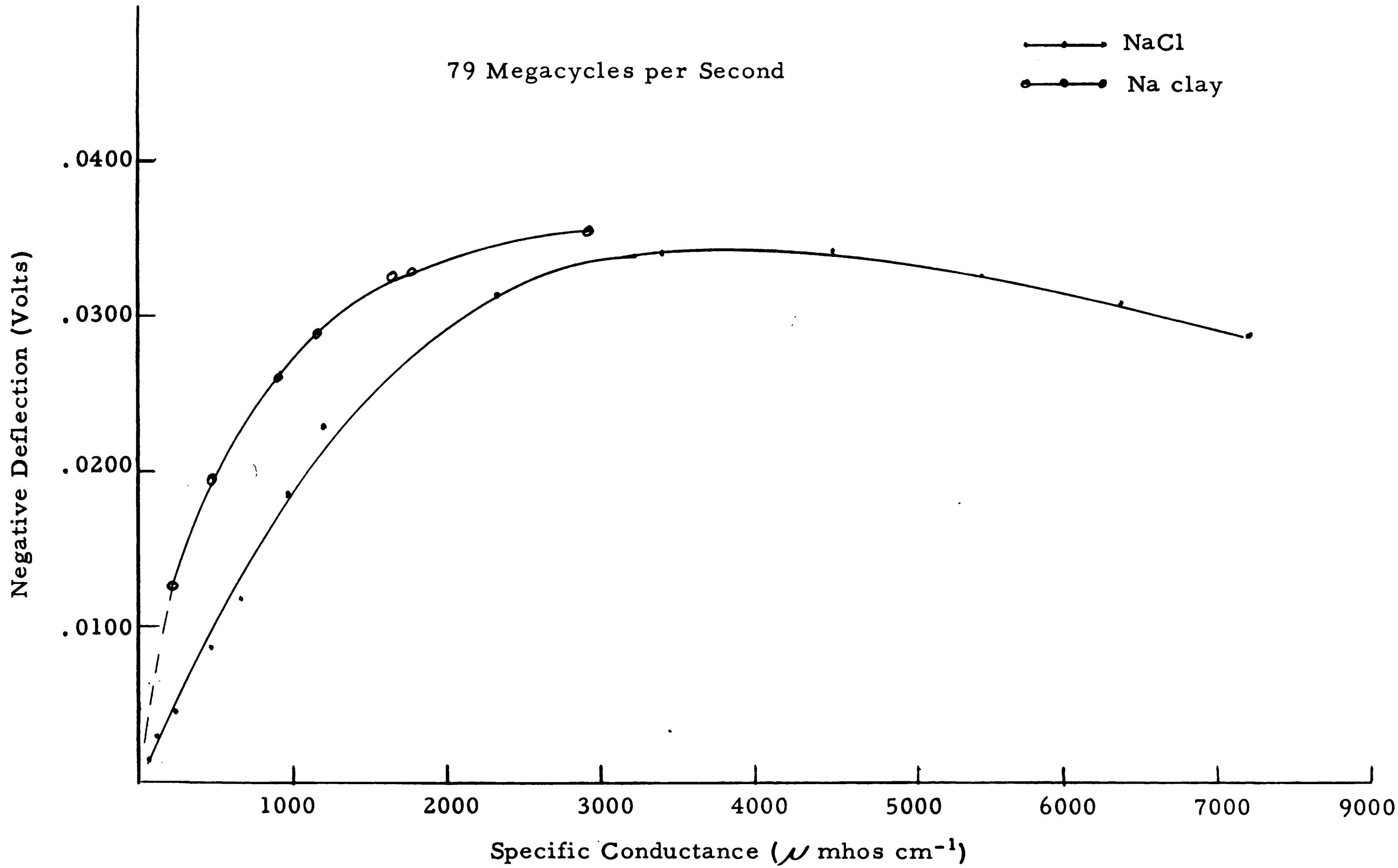


Figure 21. The relationship of high frequency response to the specific conductance of Na clay suspensions and sodium chloride solutions at seventy-nine megacycles per second.

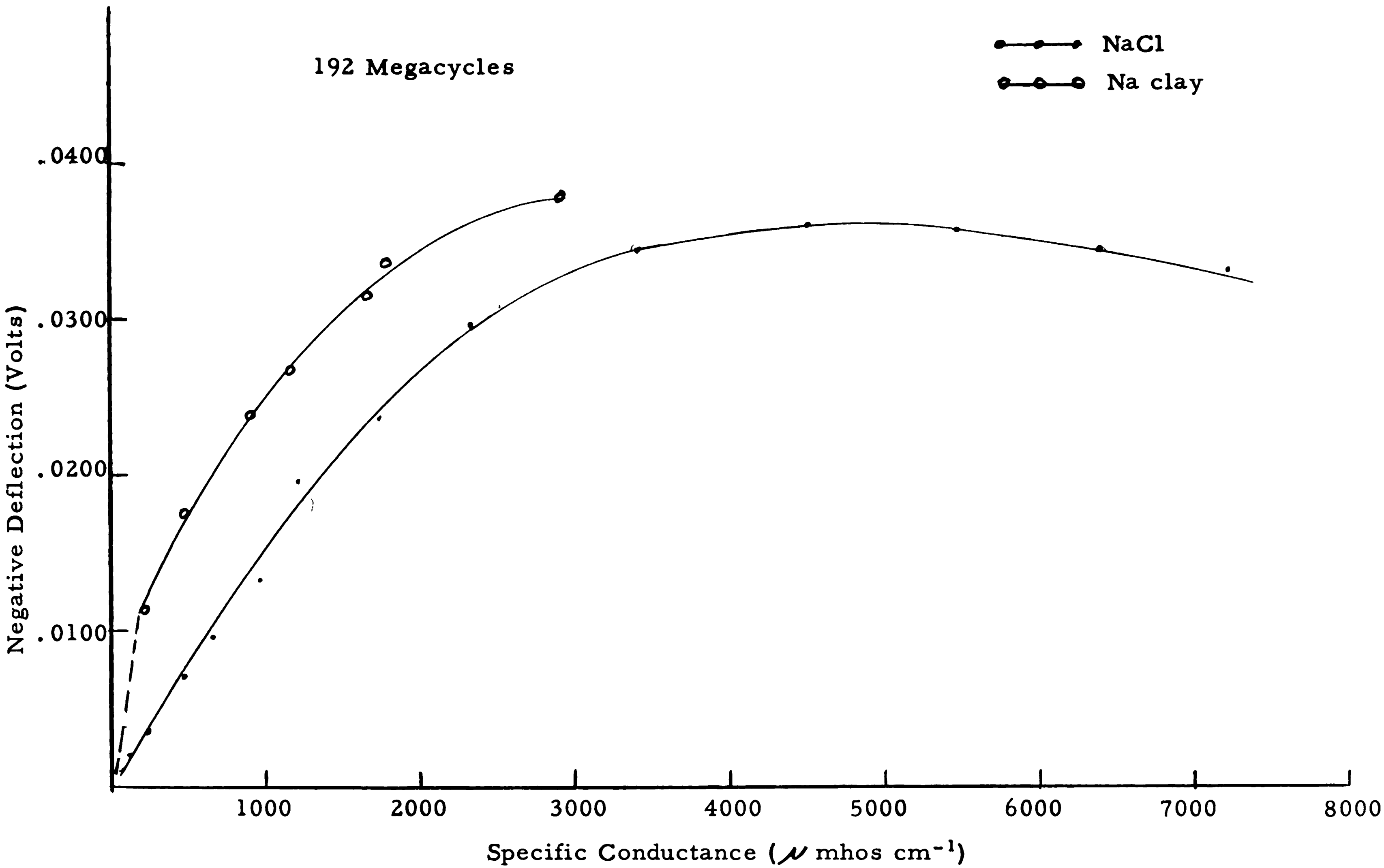


Figure 22. The relationship of high frequency response to the specific conductance of Na clay suspensions and sodium chloride solutions at one hundred ninety-two megacycles per second.

Six frequencies; 13, 30, 44, 57, 79 and 192 megacycles per second were used in this experiment. Sodium chloride and potassium chloride were the electrolytes used. The results show that the electrolyte solutions behaved similarly to those that Reilley and McCurdy (1953) used. In plotting high frequency response as a function of specific conductance all electrolytes fall on the same curve. However, the clay suspension curves varied from those of the electrolyte solutions. The clay suspensions showed greater response with respect to specific conductance than did the electrolyte solutions. At the lower frequencies the maxima of the clay suspension curves fell below those of the electrolyte curves. However, as the frequency was increased, the difference in the maxima became less until there was essentially none.

The results obtained for the second part of high frequency conductance measurements are presented in Figures 23 through 34. These data show the effect of the type of cation associated with the clay on the response of high frequency conductance. The electrolyte solutions, sodium chloride and calcium chloride, were also used in order to check the previous results. The Wyoming bentonite clays included those saturated with sodium, potassium, lithium, calcium, barium, magnesium, hydrogen and aluminum. In these interpretations the hydrogen clays were not used because of the combination of aluminum and hydrogen ions in the suspensions due to changes in the mineral composition of the hydrogen clays. It was found that the specific conductance measurements of the aluminum clays were extremely erratic due to the effect of flocculation. Therefore, the aluminum clays were also not included in the interpretations of high frequency conductance measurements. The 13, 44, 79 and 192 megacycles per second frequencies were employed for this part of the experiment. The results showed a difference between

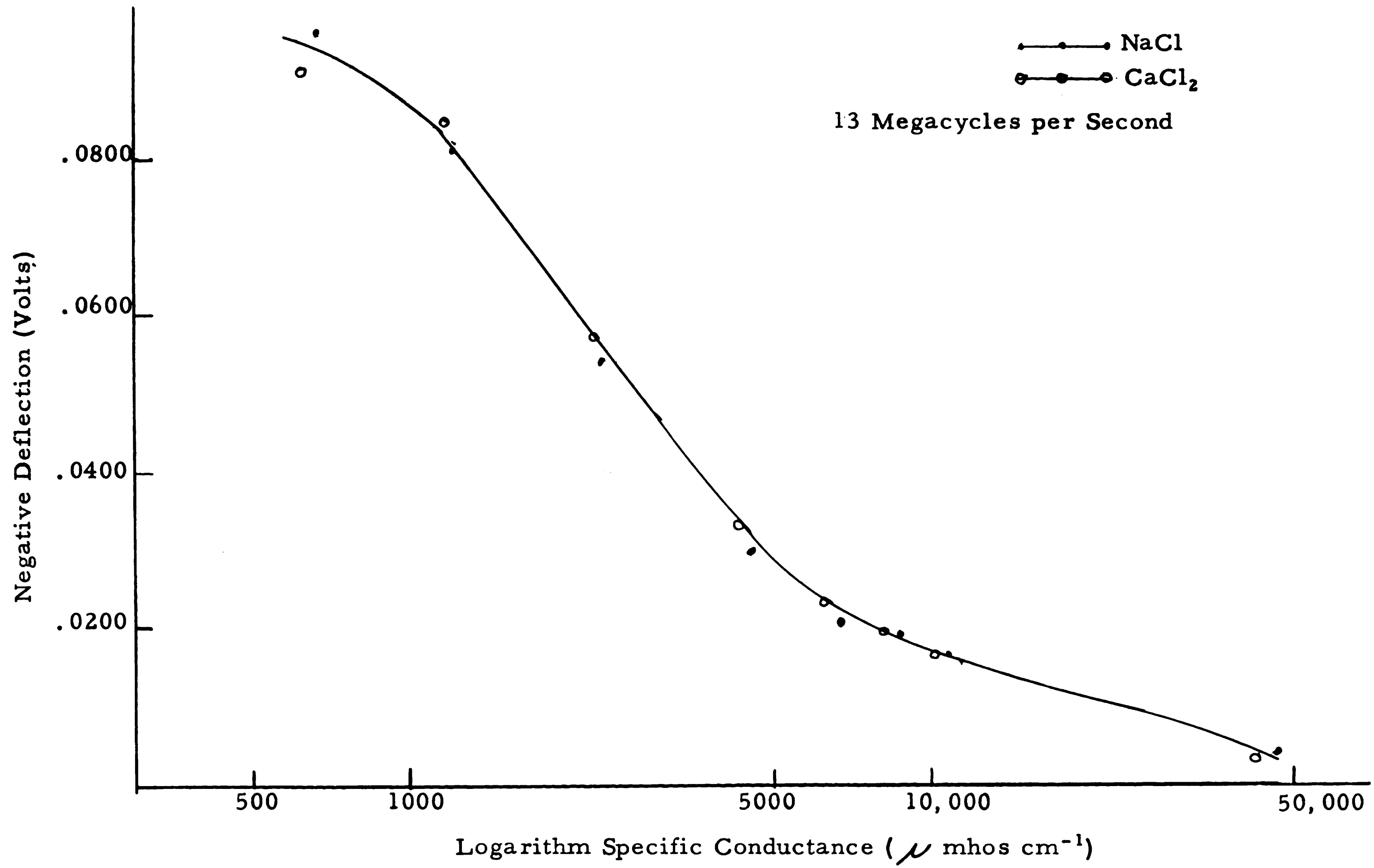


Figure 23. The relationship of high frequency response to the specific conductance of sodium chloride and calcium chloride solutions at thirteen megacycles per second.

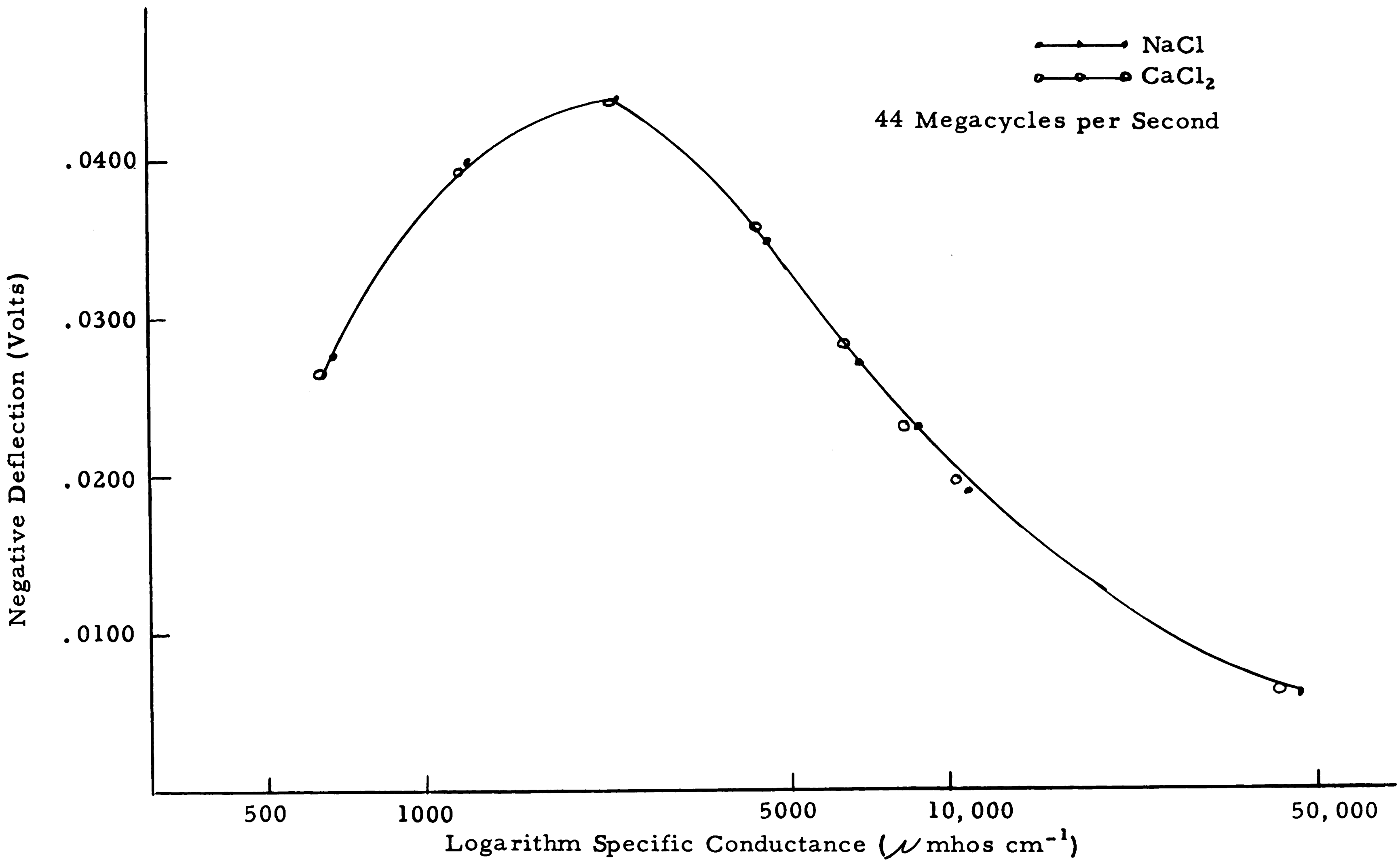


Figure 24. The relationship of high frequency response to the specific conductance of sodium chloride and calcium chloride solutions at forty-four megacycles per second.

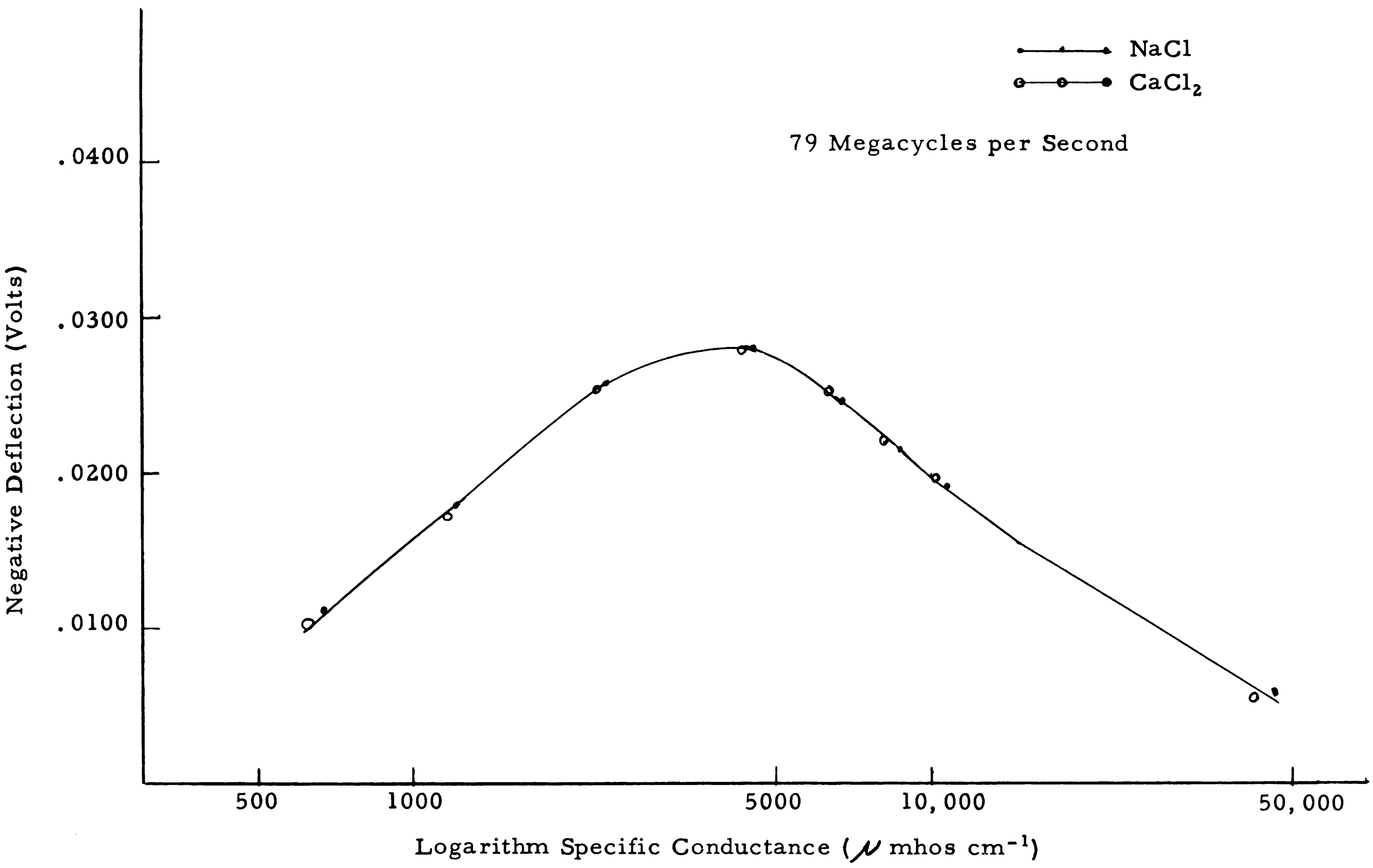


Figure 25. The relationship of high frequency response to the specific conductance of sodium chloride and calcium chloride solutions at seventy-nine megacycles per second.

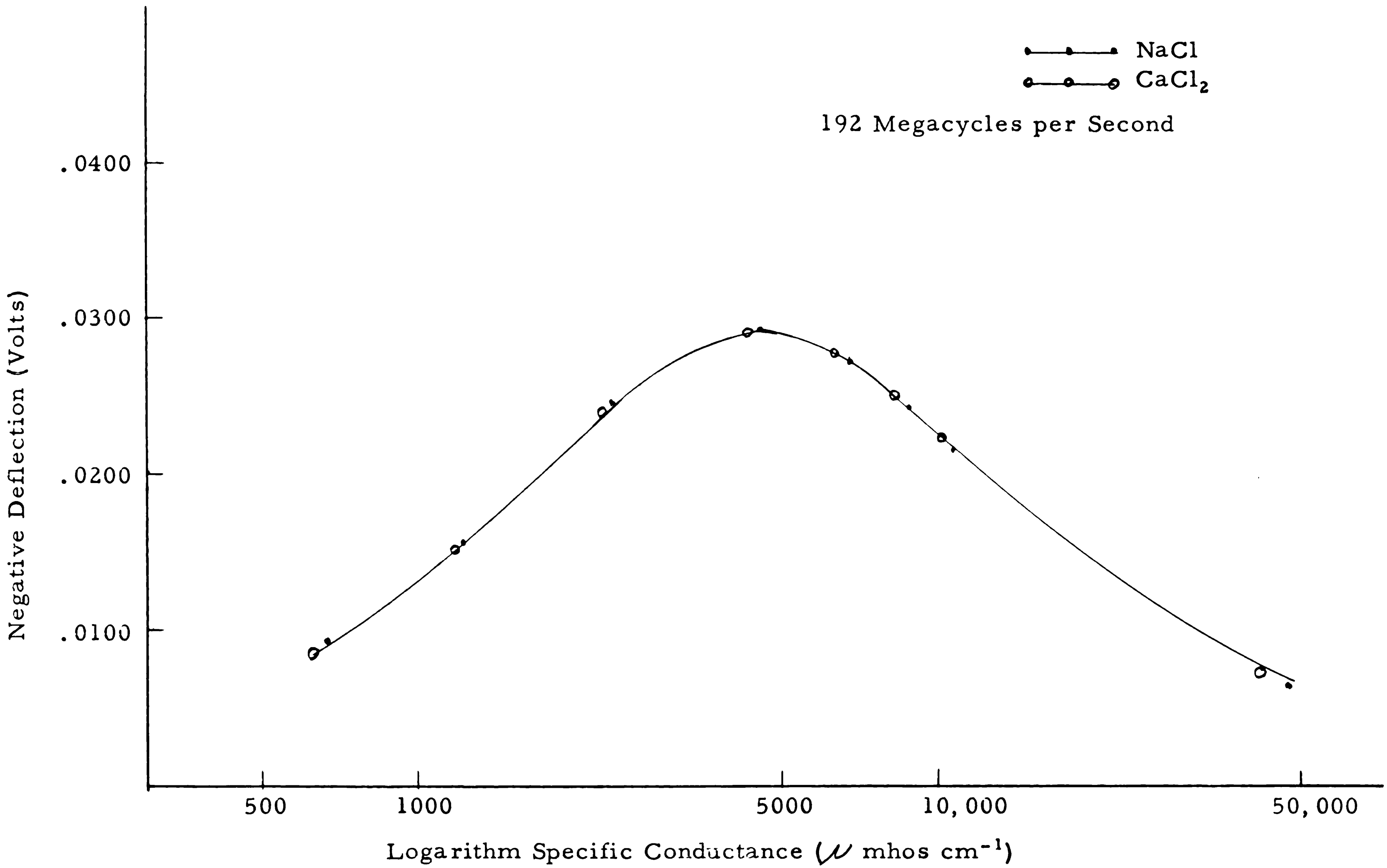


Figure 26. The relationship of high frequency response to the specific conductance of sodium chloride and calcium chloride solutions at one hundred ninety-two megacycles per second.

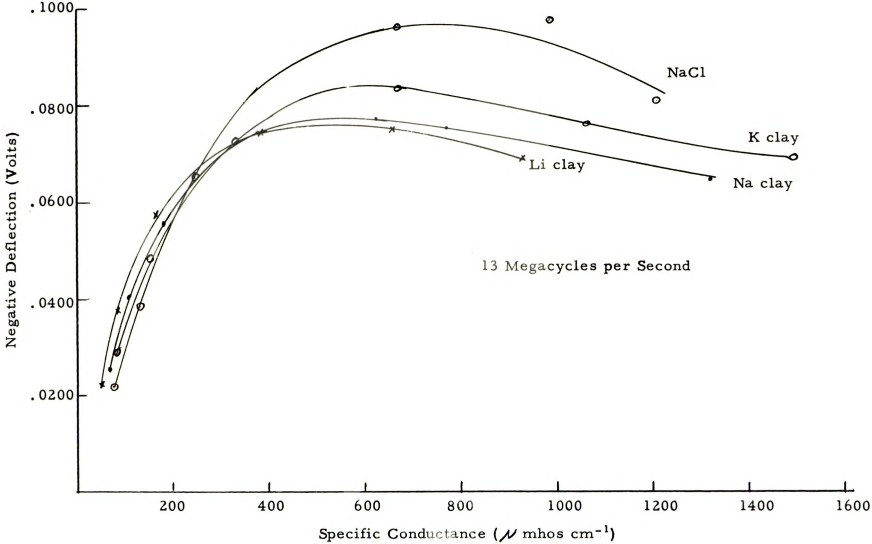


Figure 27. The relationship of high frequency response to the specific conductance of monovalent cation clay suspensions and sodium chloride solutions at thirteen megacycles per second.

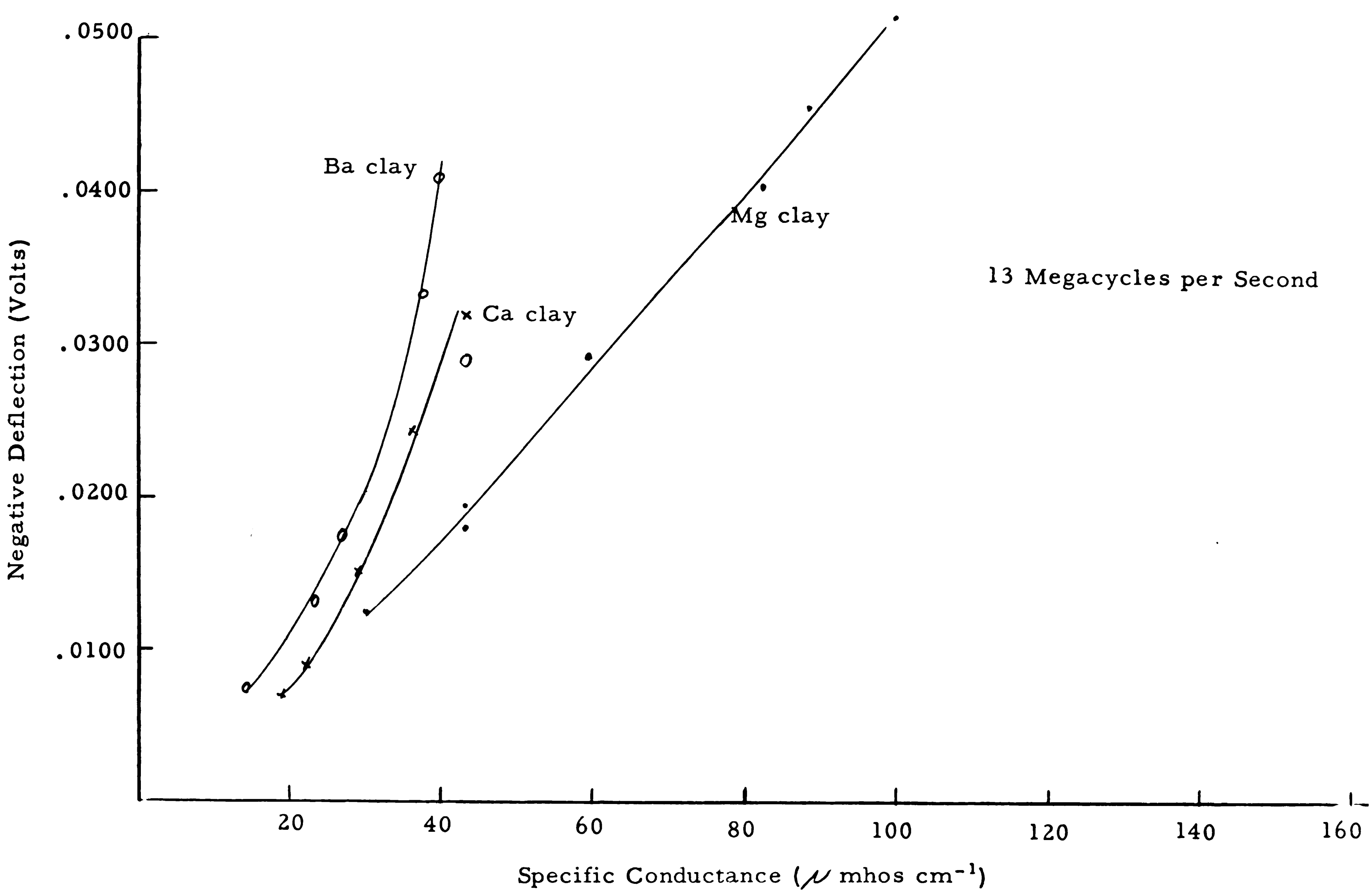


Figure 28. The relationship of high frequency response to the specific conductance of divalent cation clay suspensions and sodium chloride solutions at thirteen megacycles per second.

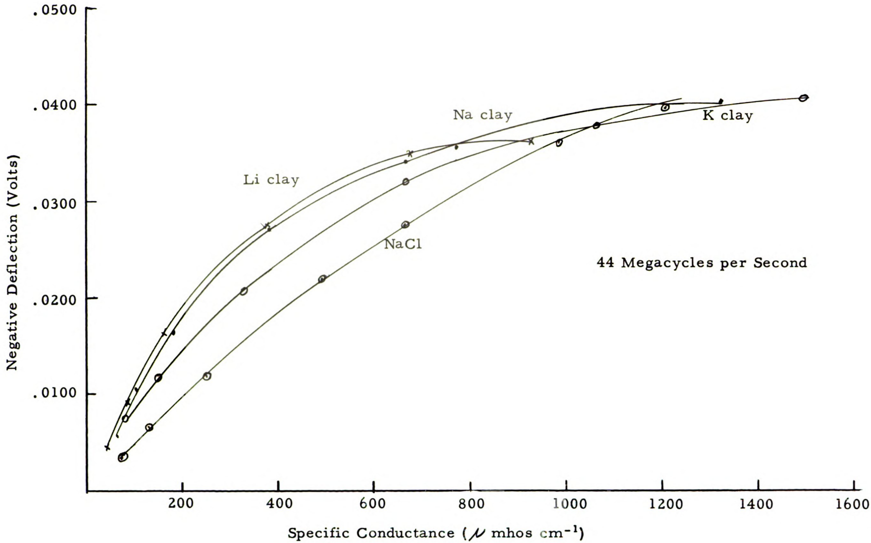


Figure 29. The relationship of high frequency response to the specific conductance of monovalent cation clay suspensions and sodium chloride solutions at forty-four megacycles per second.

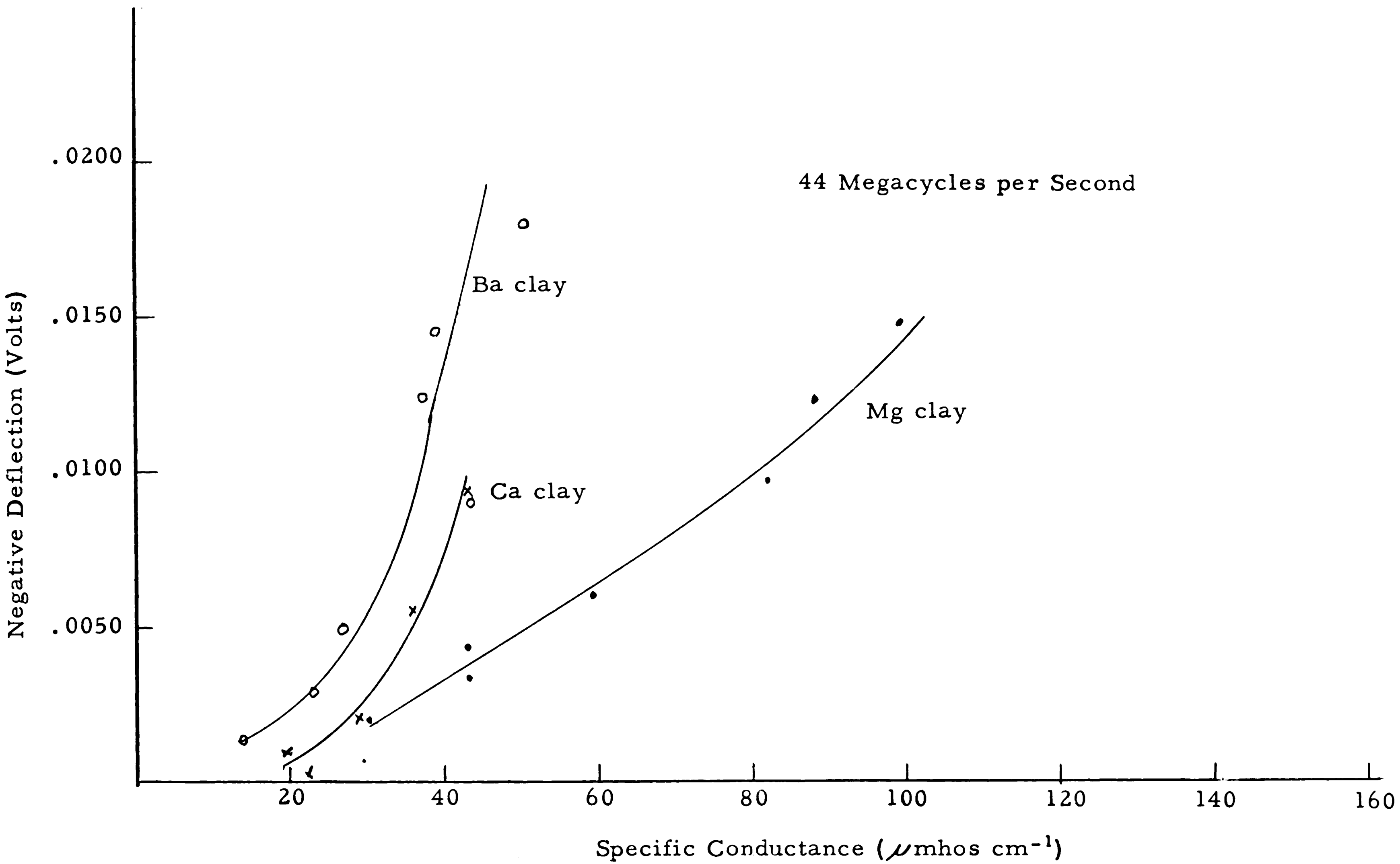


Figure 30. The relationship of high frequency response to the specific conductance of divalent cation clay suspensions and sodium chloride solutions at forty-four megacycles per second.

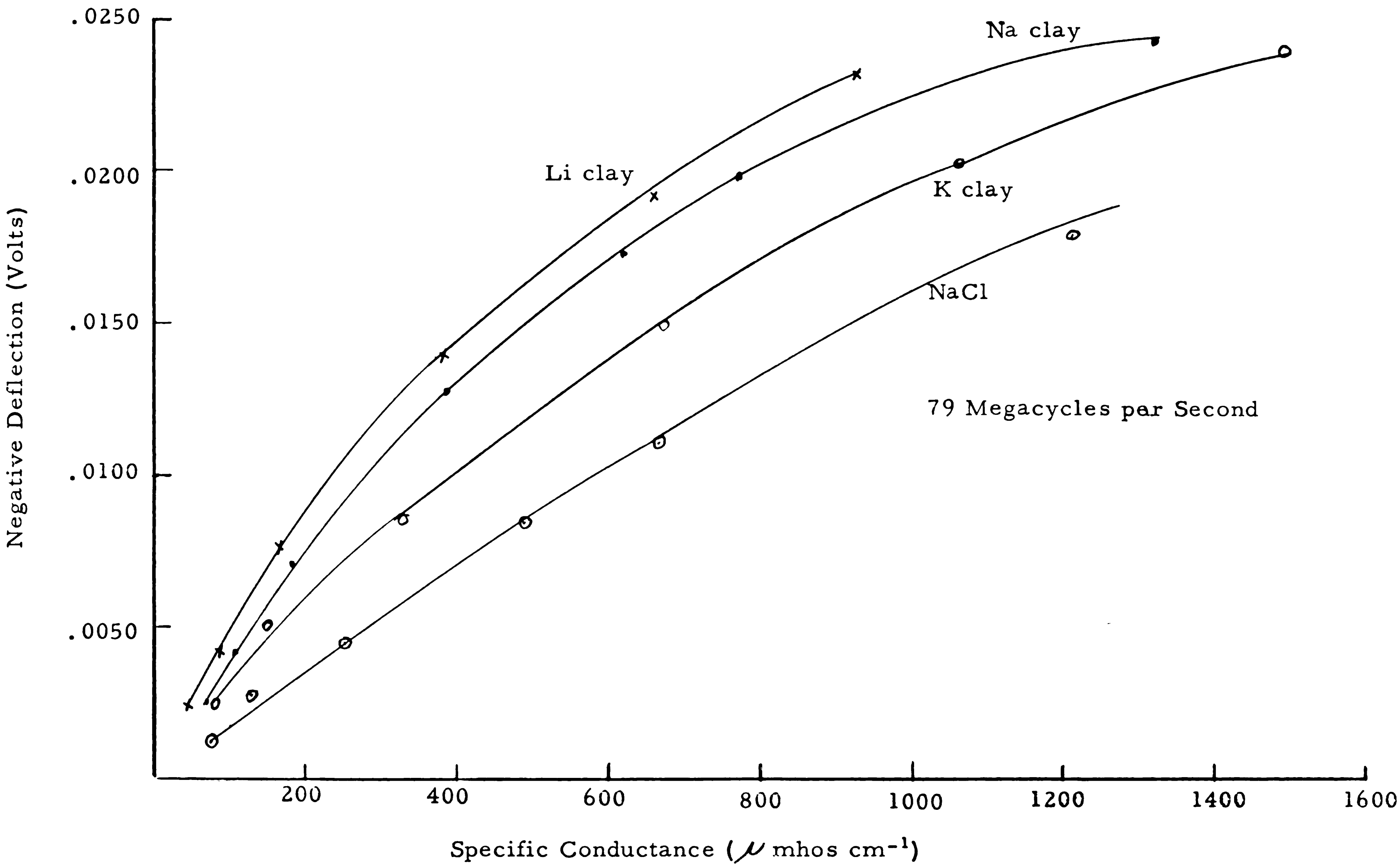


Figure 31. The relationship of high frequency response to the specific conductance of monovalent cation clay suspensions and sodium chloride solutions at seventy-nine megacycles per second.

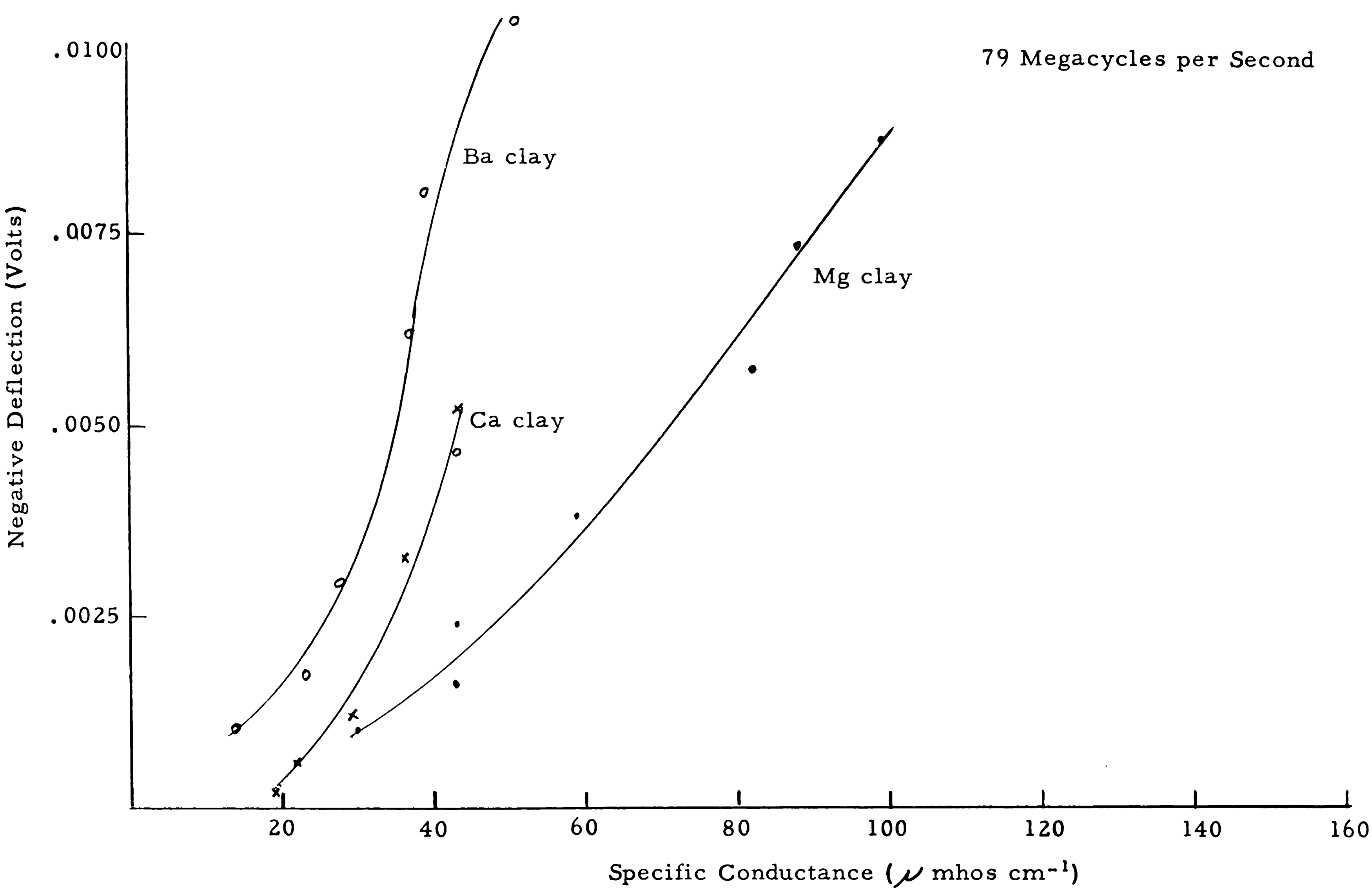


Figure 32. The relationship of high frequency response to the specific conductance of divalent cation clay suspensions and sodium chloride solutions at seventy-nine megacycles per second.

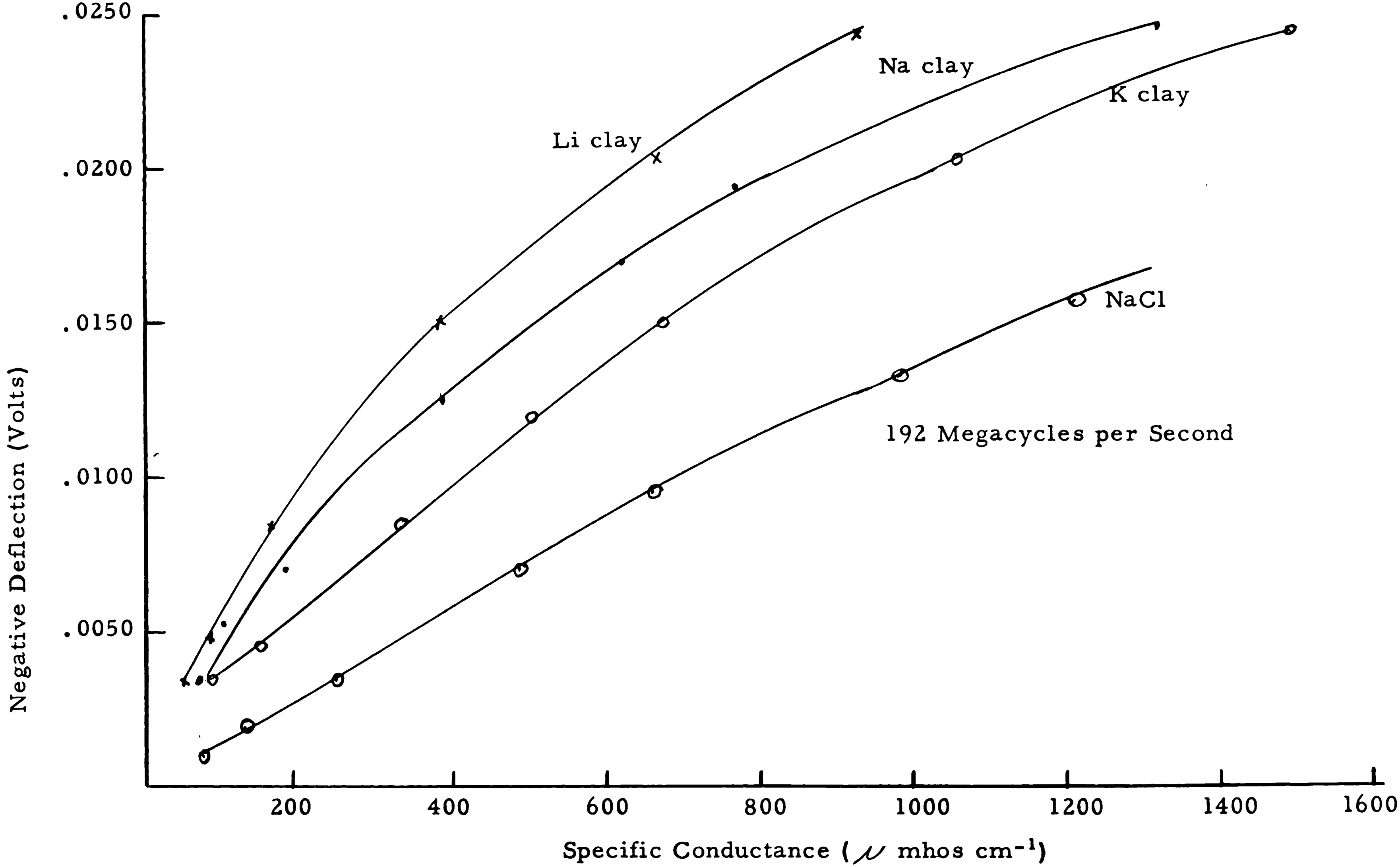


Figure 33. The relationship of high frequency response to the specific conductance of monovalent cation clay suspensions and sodium chloride solutions at one hundred ninety-two megacycles per second.

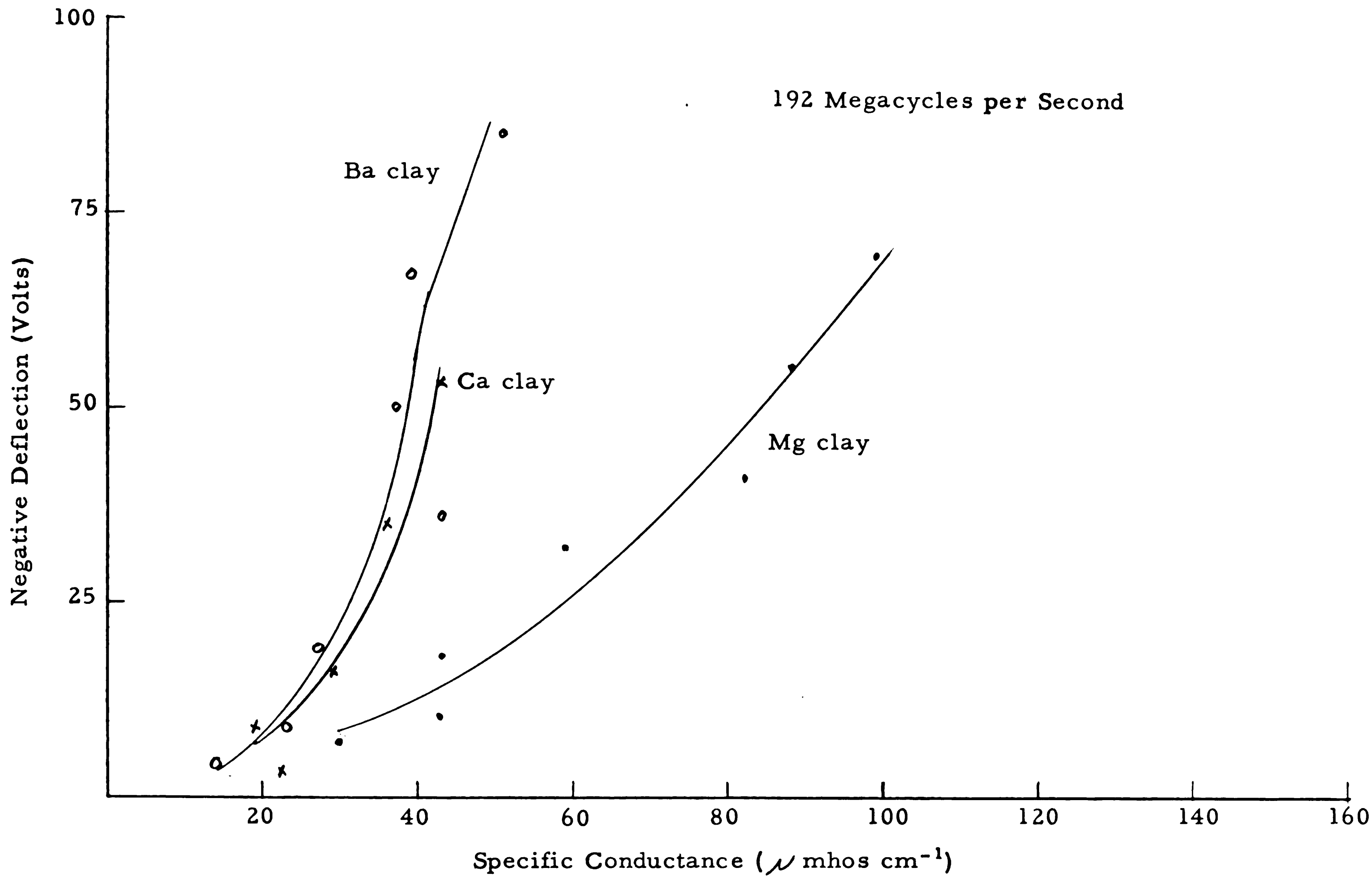


Figure 34. The relationship of high frequency response to the specific conductance of divalent cation clay suspensions and sodium chloride solutions at one hundred ninety-two megacycles per second.

the different types of clays used. The response in decreasing order to these different types of clay was as follows:

Ba clay > Ca clay > Mg clay > Li clay > Na clay > K clay.

The third part of the high frequency conductance involved the response to a change in moisture, butanol, and octanol in clay-sand mixtures containing five and ten percent clay. The results, obtained over a low liquid range, zero to six percent by weight, may be found in Tables X, XI and XII. The liquid was added to the clay-sand mixtures and allowed to equilibrate for one week, at which time percent liquid and high frequency conductance measurements were taken. The assumption was made that one week was time enough for the liquid to equilibrate in an unsaturated condition, which is not strictly true. The results show that the response was different at different clay contents for both the water and the alcohols, the five percent clay mixture giving a greater response than the ten percent clay mixture. A maximum was reached in all cases, though the alcohols gave much greater variability than did the water. No explanation is given for this variability. The response to changes in amount of water was much greater than the response to changes in alcohol content.

An attempt was made to measure the response of high frequency conductance to moisture changes for clay-sand mixtures of five, ten and fifteen percent clay over the range of moisture which is considered available to plants. The porous plate and pressure membrane methods were used to obtain the moisture in this range. The variability of the results was such that no conclusions could be drawn.

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Discussion

The relationship of high frequency conductance to specific conductance of the clay suspensions was found to differ from the response of the ordinary electrolyte solutions. This deviation can be explained on the basis of the dependence of capacitance and conductance of colloidal systems on frequency. References are given by Kortüm and Bockris (1951) on the dependence of conductance, and by Overbeek (1952) on the dependence of capacitance on frequency.

At high frequencies, as the frequency is increased, the capacitance or measured dielectric constant decreases. This phenomenon can be explained on the basis that as the frequency is increased the charged particles have less time to complete their displacement before the a.c. frequency cycle reverses its field; thus less polarization takes place causing a decrease in the capacitance or measured dielectric constant of the suspension. The asymmetry of the double layer may not develop to its fullest extent in this frequency range, which, in turn, would decrease the amount of polarization.

The dependence of conductance on frequency is known as the dispersion of conductance or the Debye effect. This effect can be attributed to the change in f_λ, "Conductance Coefficient," with a change in the frequency of the applied field. The "Conductance Coefficient" which is defined as the ratio of the measured equivalent conductance to the ideal value which according to Kortüm and Bockris (1952) was introduced by Bjerrum into equation (1)

$$\frac{\Lambda_v}{\Lambda_\infty} = \alpha \; f_\lambda \qquad (1)$$

where Λ_v is the measured equivalent conductance, Λ_∞ is the equivalent conductance at infinite dilution, and α is the degree of dissociation. This coefficient was introduced to take into consideration the effect of concentration on the ionic mobility of electrolyte solutions. The mechanism of the Debye effect can be explained by considering the ionic atmosphere in an electrolyte solution.

In an a.c. field a central ion of an ionic atmosphere changes its direction of motion with the change in the direction of the cycles of the applied field. At low frequencies the mobility of the ion is retarded because of its ionic atmosphere. When the frequency becomes very high the central ion changes direction so quickly that there is little chance for the ionic atmosphere to retard the motion of the central ion. Thus an increase or dispersion of conductance occurs.

In the case of clay suspensions the retarding force on exchangeable cation may be expected to vary as the distance of these cations from the surface of the clay particles varies. The closer the exchangeable cation is to the clay particle, the greater the force of attraction of the ion to the clay. Another possible explanation of retarding forces may be on the basis of increased viscosity of water near the clay particle, thus creating a greater frictional force for the exchangeable cations to overcome. A discussion of this point of view is made by Low and Lovell (1959).

The electrical potential exerted by the clay mineral on associated ions is described in terms of an exponential function. As the distance from the clay particles increases the force which retards the movement of ions decreases exponentially. A differential in the mobility of the ions in the double layer thus occurs. This differential in the mobility of ions gives a measured conductance at low frequency which is much lower than would be expected if all the ions were free of any retarding force. If the frequency is increased to a point where the ions move only a very short distance in following the alternating field, then these ions do not have to overcome the retarding force or at least only a portion of it. This causes an overall increase in the mobility of the ions; thus increasing the conductance of the suspension.

The high frequency conductance measurements are interpreted in terms of the parallel equivalent circuit. Since the equivalent circuit is the same as that used in the capacitance measurements, the admittance is also the same. Thus, the high frequency conductance term is given as

$$Gp = \frac{1}{R_p} = \frac{k\ \omega^2 C_1^2}{k^2 + \omega^2 (C_1 + C_2)^2} \qquad (2)$$

where the symbols are the same as those found in the discussion in Chapter III. However C_1 refers to the capacitance of the glass walls instead of the paraffin-beeswax mixture.

By differentiating equation (2) and setting the results equal to zero, Reilley (1954) found that the position of the peak is dependent on the frequency, the capacitance of the cell walls and capacitance of the solution in the following manner.

$$k \text{ peak or } k \text{ minimum} = \omega (C_1 + C_2) \qquad (3)$$

where k peak refers to the specific conductance at the peak of the high frequency conductance curve and k minimum refers to the specific conductance at the minimum of the high frequency parallel resistance curve.

Furthermore; Reilley (1954) found that

$$G \text{ peak} = \frac{\omega C_1^2}{2 (C_1 + C_2)} \qquad (4)$$

or

$$R \text{ minimum} = \frac{2 (C_1 + C_2)}{\omega C_1^2} \qquad (5)$$

by substituting equation (3) into equation (2) where G peak is the high frequency conductance value at the maximum and R minimum is the high frequency resistance value at the minimum.

The relationship of high frequency conductance to specific conductance of the electrolyte solutions follows the theoretical and experimental results of Reilley and McCurdy (1953). Since the voltage measured is directly related to the input resistance of the oscillation circuit, results obtained should follow equation (4) and equation (5). Figures 14, 15 and 16 show that as the frequency increases the low frequency conductance (specific conductance) at the peak or at the minimum also increases, which bears out equation (3). Equation (5) shows a decrease in high frequency resistance with an increase in frequency. This is also shown to be true in Figures 14, 15 and 16.

Even though the clay suspension curves deviate from those of the electrolyte curves, they can be explained on the basis of equation (3) and (5). From equation (5) it can be seen that if the clay curves are compared to the electrolyte curves for the same frequency, then any difference between the minima will be due to the capacitance, C_2. Since the minimum of the suspension curves falls below (more positive) that of the electrolyte curves, the capacitance of the clay suspension is indicated to be greater than that of the electrolyte solutions. This would be expected on the basis of an added polarization due to the asymmetry of the double layer of the colloidal particles at high frequencies. At the higher frequencies the minima of the clay curves are as great or slightly greater than the minima of the electrolyte curves. This suggests that as the frequency is increased further the double layer loses its asymmetry because of the rapid reversal of the alternating field.

In comparing the clay suspension curves to the electrolyte curves on the basis of equation (3) the results indicate that the capacitance of the clay suspensions is less than that of the electrolyte solutions because the k minimum of the clay curves is to the left of the k minimum of the electrolyte curves. This is apparently contradictory to equation (5). However, if the dependence of conductance on frequency is taken into consideration, then the data should follow both equation (3) and equation (5). This can be explained on the basis that the high frequency field sees more apparent free ions in the clay suspension than does the low frequency field. Therefore, if the specific conductance could be measured for the same number of apparent free ions as seen by the high frequency field, then the k minimum of equation (3) would be greater than that actually observed. This indicates that the k minimum should be at a high k value than is actually shown in Figures 17 through 22. Since equation (3) predicts that the k minimum value for the clay suspensions should be to the right of the k minimum value for the electrolyte solution on the basis of the capacitance of the clay systems, this suggests that the increase in conductance at high frequency is actually greater than that which is shown in comparison of the clay system with pure electrolytes.

The results of the different kinds of cation saturation of the clay show that the high frequency conductance compared to the specific conductance differs with the kind of cation associated with the Wyoming bentonite. These responses are all based on the deviation from high frequency-low frequency conductivity curves of electrolytes. Figures 27 through 34 show the following response in decreasing order:

Ba clay > Ca clay > Mg clay > Li clay > Na clay > K clay.

It was observed that the difference in high frequency response between the kinds of cation-saturated clays increased with an increase in frequency. However, the ratio of the difference in high frequency response between the kinds of cation-saturated clays stayed approximately the same.

In order to explain this phenomenon, high frequency conductance response was plotted against concentration (equivalents per liter) for the sodium chloride solutions and for sodium clay suspensions. Thus, as indicated in Figure 35, as the frequency increases, the difference between the electrolyte curve and the clay suspension curve decreases. This is assumed to be due to a reduction of the displacement of ions. The calculated distance traveled by the ions at a frequency of one megacycle per second, is 0.00194, 0.00260 and 0.00381 Å per half cycle for lithium, sodium and potassium, respectively. This might suggest that all the retarding force encountered by ions at low frequency should be negligible at one megacycle per second. However, as the distance from the surface of the clay decreases to a small value the force with which the cations are held by the clay should be quite strong. Anderson and Low (1958) estimated the force near the clay surface to be of large magnitude. Therefore, it does not seem improbable that some of the ions are retarded at very high frequencies even though the movement of ions is very small.

Since this experiment was not designed to explain why a difference in high frequency response occurred for the various cation-saturated clays, several explanations are given based on various concepts of the structure of clay and its environment.

The sequence of the high frequency response of the different kinds of cation-saturated clays may be explained on the basis of the viscosity of the water near the surface of the clay. It was postulated in a review by Low and Lovell (1959) that the structural development in the adsorbed water near the clay surface is enhanced by increased ionic dissociation from the clay. The disruptive effect of the ions is less when they are distributed through a relatively large volume than when they are concentrated at the surface where the structure is "anchored."

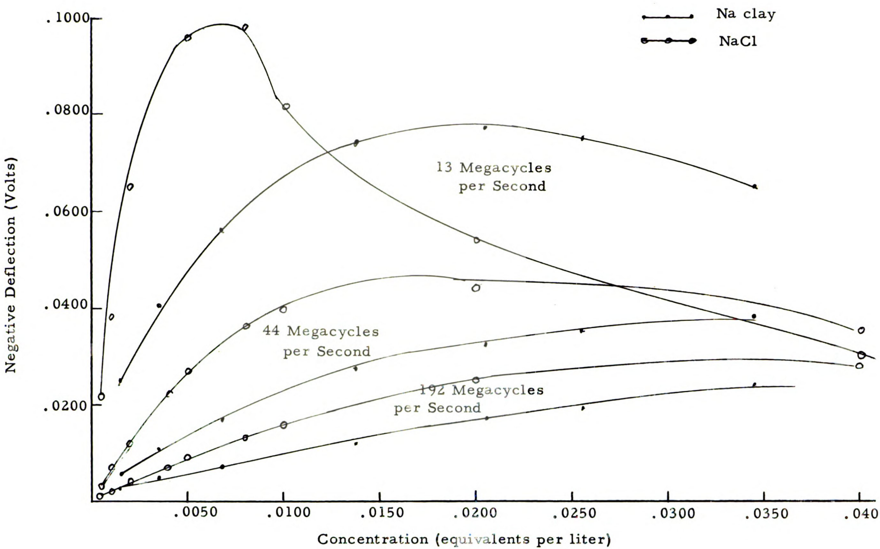

Figure 35. The relationship of high frequency response to the concentration of Na clay suspensions and sodium chloride solutions at thirteen, forty-four and one hundred ninety-two megacycles per second.

Based on activity measurements, Marshall (1949) found the fraction of the ions active to be potassium > sodium > calcium for Wyoming bentonite clay. Therefore, the potassium was considered to be the most dissociated while calcium was considered to be the least dissociated. Thus the viscosity of the adsorbed water would be greatest for the K clay and least for the Ca clay, if the argument in the preceding paragraph is accepted. This difference in viscosity coincides with the difference found for high frequency conductance measurements.

Davis (1955) reported mean ionic activities of various cation saturated Wyoming bentonite clays as related to the molality of the chloride of the different cation species associated with the clay. The order of mean ionic activities for the different cation species was found to depend on the particular sample of Wyoming bentonite used. For one set of monoionic clays the order of mean ionic activities was potassium > sodium > lithium. For another set of monoionic clays the order of mean ionic activities was just the reverse.

The order of mean ionic activities for the first set of monoionic clays follows the order for the high frequency conductance measurements if the response is based on the viscosity of water as postulated by Low and Lovell (1959). It is assumed that the mean ionic activities are a measure of the relative dissociation of the cations adsorbed by the clays.

The order of the mean ionic activities of the divalent cations associated with Wyoming bentonite as reported by Davis (1955) did not follow the order of divalent cation clays obtained by the high frequency response.

The difference in high frequency response for the various cation-saturated clays may also be based on the concept of mobility. The order of mobility at high frequencies would be different from the order of mobility of cations in electrolyte solutions. Work by Low (1958) indicates that the order of mobility of cations associated with clays do differ from the order of mobility of cations in electrolyte solutions.

A possible reason for the greater high frequency response in the case of divalent cation-saturated clays as compared to monovalent cation clays is that at the same specific conductance a larger number of divalent ions are present in the suspensions than monovalent ions because of a greater concentration of divalent cation-saturated clay. Therefore the high frequency response would be expected to be greater.

Another possible explanation for the difference in high frequency response for the various cation-saturated clays may be based on the thickness of the double layer of the clay particles. The thickness of the double layer of the clay particles may be estimated from the electrokinetic or zeta potential (ζ), which is defined as the work done in moving a unit charge from the inner boundary of the double layer to a remote point in the bulk of the solution. Marshall (1949) gives the relationship between the zeta potential (ζ) and thickness of the double layer by the following equation:

$$\zeta = \frac{\pi d \sigma}{D} \qquad (7)$$

where ζ is the zeta potential, d is the thickness of the double layer, σ is the surface density of charge and D is the dielectric constant.

Work by Baver (1929) showed that the order of zeta potential for different cation saturated clays was Li clay > Na clay > K clay. If the surface density of charge and the dielectric constant are assumed to be constant, then the Li clay would have the greatest double layer thickness while the K clay would have the least double layer thickness. On this basis the micelle of the Li clay would contain the greatest number of ions and the micelle of K clay would contain the least number of ions. Therefore, the high frequency response of the Li clay would be greater than the high frequency response of K clay. On this same basis the thickness of the double layer of the divalent cation saturated clays would be Ba clay > Ca clay > Mg clay.

It is also observed from the high frequency response of the different kinds of monovalent cation-saturated clays that there are slight but definite differences in the capacitance of the kinds of cation-saturated clays. Equation (5) indicates that the conductance at the peak is determined by the magnitude of the capacitance; the greater the conductance, the smaller the capacitance. The experimental curves in Figure 27 when applied to equation (5) indicate that the capacitance of the monovalent cation-saturated clays follow this decreasing order:

Li clay > Na clay > K clay.

Work by Marshall (1956) indicates that the clay particles themselves possess a certain mobility and so contribute to the specific conductance measurements of clay suspensions. The effect of high frequency on the conductance of the clay particles themselves can not be explained on the basis of this investigation. However, it seems reasonable that as the frequency increases an increase in the conductance of the particles would occur until a critical frequency is reached where the particles can no longer follow the alternating field because of their large mass. The clay particles would be expected to contribute very little to the high frequency conductance in the megacycle range.

The results for the clay-sand mixtures show that the high frequency response depends on variations in water, butanol and octanol contents. The results for the clay-sand mixtures also show that the high frequency response is greater for the five percent clay mixtures than for the ten percent clay mixtures at the same liquid concentration. A minimum was obtained in all cases; however, water gave the greatest deflection while octanol gave the least deflection.

The fact that a difference in response was obtained for the five percent clay mixtures compared to the ten percent clay mixtures indicates that the amount of clay has an effect on high frequency conductance measurements, but the reason for this effect is not known. The specific conductance of the mixtures would have to be known, but this could not be measured at such low liquid concentrations.

Since the minimum does not depend on the specific conductance, equation (5) predicts that the water mixtures have the largest capacitance while the octanol mixtures have the lowest capacitances. The dielectric constants of the pure liquids are 3.4, 7.8 and 78.5 for octanol, butanol and water respectively. Therefore, the results obtained for capacitances are as expected.

The following conclusions can be drawn from the high frequency conductance data:

1) The capacitance and conductance of clay suspensions as compared to those of electrolyte solutions is dependent on the frequency of the applied electric field.

2) At the lower frequencies employed (13, 30, and 44 megacycles per second), the capacitance of the clay suspension is greater than the capacitance of electrolyte solutions. At the higher frequencies employed (57, 79, and 192 megacycles per second) the capacitance of the clay suspensions is similar to that of the electrolyte solutions. In the case of the monovalent cation saturated clays the order of capacitance is Li clay > Na clay > K clay.

3) The high frequency response based on specific conductance is greater for the clay suspensions as compared to that of the electrolyte solutions. The high frequency response based on

specific conductance also differs with the kind of cation saturated Wyoming bentonite clay. The order of high frequency response is as follows:

Ba clay > Ca clay > Mg clay > Li clay > Na clay > K clay.

4) At low concentrations of liquids in clay-sand mixtures the capacitances of water, butanol and octanol in clay-sand mixtures follow the same order as the dielectric constants of the pure liquids. The order is as follows: water > butanol > octanol.

CHAPTER V

SUMMARY

The results obtained for the dielectric properties and high frequency conductance of Wyoming bentonite may be summarized as follows:

1) The capacitance of the clay suspensions was found to be dependent on the frequency at which the measurements were made.

2) In the kilocycle frequency range the capacitance of all the base saturated clays showed the same relationship to the specific conductance of the clay suspensions.

3) In the megacycle frequency range the capacitance of the monovalent cation clays followed this order:

   Li clay > Na clay > K clay.

4) The capacitances of the clay suspensions were greater than those of the electrolyte solutions in the low megacycle frequency range. This difference between the capacitances of the electrolyte solutions and the capacitances of clay suspensions diminished as the frequency was increased.

5) The high frequency conductance of the clay suspensions was found to be dependent on the frequency at which the measurements were made.

6) The high frequency conductances of the clay suspensions were greater than those of the electrolyte solutions at similar specific conductances (low frequency).

7) The high frequency conductance varied with the cation associated with the clay and was found to follow this order:

Ba clay > Ca clay > Mg clay > Li clay >
Na clay > K clay.

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APPENDIX

TABLE I

DEPENDENCE OF pH AND SPECIFIC CONDUCTANCE ON THE MILLIEQUIVALENTS OF NaOH ADDED TO HYDROGEN SATURATED WYOMING BENTONITE

Meq. NaOH per 100 gms. of clay	pH	Sp. conductance ($10^2\mu$ mhos cm^{-1})	Meq. NaOH per 100 gms. of clay	pH	Sp. conductance ($10^2\mu$ mhos cm^{-1})
0.00	3.50	3.10	80.83	6.20	1.02
8.12	3.55	2.95	84.04	6.71	1.03
16.24	3.60	2.67	87.25	7.63	1.20
24.36	3.62	2.35	90.46	8.70	1.40
32.48	3.66	2.10	93.67	9.40	1.75
40.60	3.88	1.80	96.88	9.70	2.20
48.73	4.00	1.53	100.09	9.90	2.65
51.94	4.18	1.42	103.31	10.00	3.05
55.15	4.27	1.33	106.52	10.12	3.45
58.36	4.30	1.21	109.73	10.19	4.05
61.57	4.53	1.09	112.94	10.28	4.55
64.78	4.95	0.98	121.06	10.40	5.70
67.99	5.40	0.98	129.18	10.50	7.05
71.20	5.55	0.98	145.33	10.65	9.70
74.41	5.72	0.98	161.47	10.80	12.50
77.62	6.00	0.98			

TABLE II

FREQUENCY DEPENDENCE OF CAPACITANCE OF WYOMING BENTONITE CLAYS AND ELECTROLYTE SOLUTIONS

Sample	Capacitance ($\mu\mu$ farads) Frequency (kilocycles second $^{-1}$)								
	1	10	50	100	200	300	400	500	600
					Na Cl				
.005N	68	73	74.5	74.5	70.5	68	56.5	46.5	38
.01N	68	73	74.5	74.5	70	65	54	45	38
.02N	68	74	74.5	74.5	70	65	56	47	40
.04N	68	74	74.5	74	70	64	55	47	39
.10N	66	74	74.5	74	70	65	56	47	41
1.00N	66	74	74.5	74	70	67	55	52	44
					Ca Cl_2				
.005N	68	74	74.5	74.5	70	65.5	58	50	43
.01N	68	74.5	75	74.5	70	65	58	47.5	43
.02N	67	74	75	74.5	70	65	57	49	42
.04N	68	74	75	74.5	70	65	58	50	40
.10N	68	74	75	74.5	70	65	58	50	40
1.00N	66	74	75	74.5	70	65	58	50	44
					Ca Clay				
2	66	71.5	74.5	80	106	80	54	42	33
3	66	73	75	82	100	73	54	40	33
4	65	71.5	74.5	78	105	85	61	48	38
5	66	72	74.5	76.5	96	98	66	45	36
6	65	71.5	74.5	75.5	89	95	81	50	40
7	66	73	74.5	74.5	75	79.5	79.5	65	50
8	65	73	74.5	74.5	75	80	75	65	55

Continued

TABLE II - Continued

Sample Number	Capacitance ($\mu\mu$ farads) Frequency (kilocycles second^{-1})								
	1	10	50	100	200	300	400	500	600
					Ba Clay				
2	66	71.5	74.5	80	105	69	50	40	32
3	--	71	74.5	80	106	76	50	40	31
4	66	71	74.5	77	98	75	53	43	32
5	66	71.5	74.	75	84	91	70	46	38
6	66	71	74.5	75	85	90	65	45	40
7	66	71.5	74	75	82	87	66	47	37
8	66	71	74	74.5	79.5	92	84	61	47
					Al Clay				
2	65	72	74.5	77	104	82	67	46	33
3	66	71	74.5	79	108	76	55	43	30
4	66	71	74.5	79.5	106	75	57	45	34
5	66	71	74.5	79	108	78	58	43	36
6	66	73	75	79.5	104	77	62	46	37
7	66	73	75	75.5	87	105	68	58	38
8	65	72	75	78	89	100	66	51	35
					Mg Clay				
2	66	71.5	74.5	78	105	80	54	40	31
3	66	71.5	74.5	76	95	90	67	44	31
4	66	71.5	74.5	75.5	90	97	66	43	32
5	66	72	74.5	75	83	95	75	51	42
6	66	72	74	75	79	86	89	63	46
7	66	71.5	74.5	75	75.5	84	94	69	43
8	66	72	74.5	74.5	76	80	90	64	46

Continued

TABLE II - Continued

Sample Number	Capacitance ($\mu\mu$ farads) Frequency (kilocycles second^{-1})								
	1	10	50	100	200	300	400	500	600
					Na Clay				
2	65	72	74.5	75	83	98	76	56	38
3	65	72	74.5	74.5	78	85	80	68	46
4	65	72	73.5	73.5	74	72	68	70	50
5	65	72	74	72.5	70	67	59	55	51
6	66	72	73.5	73	70	66	60	54	47
7	66	72	73.5	72.5	70	66	57	53	44
8	66	72	73.5	72.5	70	66	57	51	43
					K Clay				
2	66	73	74.5	75	82	91	83	63	44
3	66	74	75	75	76	76	75	66	50
4	66	71.5	73.5	73.5	71.5	67	63	57	49
5	66	71	73	72.5	70	68	60	54	48
6	66	71.5	73	72.5	70	65	59	52	40
7	66	71.5	73	72.5	69.5	64	57	52	46
8	66	72	73.5	72.5	70	65	56	48	45
					Li Clay				
2	65	72	74	76	93	88	65	52	37
3	65	73	74	75	79	87	72	63	45
4	65	73	74.5	74.5	75	72	66	57	48
5	65	72	74	72.5	70	67	59	55	51
6	66	72	73.5	73	70	66	60	54	47
7	64	72	73.5	72.5	70	66	57	53	44

Continued

TABLE II - Continued

Sample Number	Capacitance ($\mu\mu$ farads) / Frequency (kilocycles $second^{-1}$)								
	1	10	50	100	200	300	400	500	600
					H Clay				
2	65	71.5	74.5	80	100	66	50	38	31
3	66	72	74	74.5	75	82	78	66	45
4	66	71	73	73	71	69	67	65	52
5	66	71.5	74	73	70	65	61	55	42
6	66	72.5	74	73.5	70	65	60	55	45
7	66	72.5	74.5	73.5	70	65	59	52	46
H_2O	68	70	57	52	47	44	37	31	25

TABLE III

FREQUENCY DEPENDENCE OF RESISTANCE OF WYOMING BENTONITE CLAYS AND ELECTROLYTE SOLUTIONS

Sample	Resistance (ohms) Frequency (kilocycles second $^{-1}$)							
	10	50	100	200	300	400	500	600
					Na Cl			
.005N	7.2	15.4	16.0	15.8	15.0	15.5	13.7	12.6
.01N	6.5	15.0	15.4	15.5	14.7	13.3	14.2	13.8
.02N	5.8	15.0	15.8	15.2	14.7	14.3	13.6	13.9
.04N	6.5	15.0	15.5	15.9	14.9	14.5	12.5	13.5
.10N	5.4	15.0	15.1	15.2	14.7	14.8	13.6	12.8
1.00N	4.3	15.0	15.1	15.2	14.7	14.5	13.8	14.1
					Ca Cl_2			
.005N	6.8	15.0	15.6	15.5	14.6	13.7	14.3	13.0
.01N	6.4	14.9	15.4	15.5	14.7	14.3	13.4	13.7
.02N	5.4	14.9	15.4	15.5	14.7	14.5	13.0	13.3
.04N	5.4	14.9	15.4	15.5	14.7	13.7	13.7	13.9
.10N	5.4	14.9	15.6	15.5	14.7	14.6	13.7	13.9
1.00N	4.3	14.9	15.4	15.5	14.7	14.6	14.3	13.8
					Ca Clay			
2	11.1	21.4	21.9	24.0	35.8	22.1	22.7	22.2
3	13.7	22.7	23.2	25.2	23.6	23.3	23.1	21.7
4	11.1	19.7	20.4	22.0	20.6	20.9	19.9	21.0
5	12.2	18.6	19.8	19.9	21.1	19.3	19.5	19.0
6	7.8	17.1	19.0	19.1	18.4	19.1	19.1	17.9
7	8.7	16.7	16.7	17.0	16.0	16.0	15.9	15.0
8	8.7	17.1	17.1	17.0	16.3	16.3	15.9	15.3

Continued

TABLE III - Continued

TABLE III - Continued

Sample Number	Resistance (ohms) Frequency (kilocycles second $^{-1}$)							
	10	50	100	200	300	400	500	600
					Ba Clay			
2	12.2	24.6	25.3	26.5	25.4	24.8	23.1	23.9
3	14.8	21.4	21.9	24.0	22.0	22.0	21.5	20.5
4	10.1	19.2	20.7	22.7	20.6	20.4	19.3	19.9
5	8.0	17.2	17.6	18.4	18.0	18.2	17.3	16.8
6	11.2	17.1	18.0	18.7	18.6	18.4	17.7	17.9
7	10.0	17.2	17.4	18.1	18.3	18.1	16.9	17.2
8	9.0	17.2	17.1	17.4	17.3	17.1	17.0	15.9
					Al Clay			
2	8.8	18.6	19.9	20.4	20.4	19.5	19.0	19.3
3	11.2	21.4	22.2	23.6	23.0	22.3	22.2	21.2
4	9.0	21.4	22.0	24.0	22.3	23.2	23.4	21.1
5	8.5	19.9	20.8	22.9	21.4	21.1	21.1	19.9
6	7.6	19.1	19.6	20.7	20.7	19.8	20.8	19.8
7	4.6	17.0	17.5	17.8	19.0	16.9	16.5	16.8
8	7.7	19.5	20.4	21.5	22.3	17.8	19.4	18.2
					Mg Clay			
2	10.5	19.7	20.4	20.9	19.9	20.6	21.1	21.6
3	10.5	17.7	18.9	20.1	19.5	19.0	18.1	20.5
4	8.9	17.1	18.3	18.2	18.4	16.9	17.4	17.4
5	8.8	17.1	17.6	17.8	17.6	17.0	15.6	16.3
6	7.7	16.8	17.0	16.7	17.2	17.0	15.9	15.6
7	6.7	16.7	17.0	16.9	16.1	16.6	15.9	14.8
8	6.6	16.0	16.7	16.8	16.3	16.3	14.9	14.9

Continued

TABLE III - Continued

Sample Number	Resistance (ohms) Frequency (kilocycles second $^{-1}$)							
	10	50	100	200	300	400	500	600
					Na Clay			
2	8.9	17.1	17.4	17.7	18.4	16.8	16.2	16.8
3	8.9	16.7	17.1	16.3	16.9	16.9	15.7	15.6
4	7.1	16.0	15.2	16.4	15.9	15.2	14.3	14.3
5	6.0	15.5	16.0	15.9	15.5	14.8	14.5	14.4
6	4.4	15.6	15.7	15.9	15.7	15.1	14.7	13.6
7	6.6	15.2	16.0	15.9	15.4	14.5	14.4	14.1
8	4.4	15.2	16.0	15.9	15.2	14.0	15.0	14.5
					K Clay			
2	10.3	16.7	17.0	16.7	16.3	15.9	15.9	16.3
3	8.6	15.9	16.6	16.8	16.1	15.9	14.5	14.3
4	7.4	16.2	16.9	16.5	15.4	15.2	14.8	14.6
5	6.7	15.7	16.3	15.9	15.2	15.1	14.7	13.9
6	6.7	15.7	16.0	15.9	15.4	14.8	14.4	13.9
7	6.0	15.3	16.0	16.0	14.9	14.8	14.7	13.8
8	6.6	15.2	16.0	15.9	14.7	14.2	13.3	13.8
					Li Clay			
2	6.6	17.2	18.9	17.1	18.6	17.9	17.5	18.5
3	8.7	17.0	17.0	17.1	17.0	17.0	15.2	15.9
4	9.4	16.0	16.5	16.6	16.1	15.2	15.1	14.9
5	6.6	15.5	16.5	16.4	15.0	15.1	13.9	12.5
6	8.8	15.8	15.7	15.9	15.7	14.1	13.3	13.6
7	2.2	15.8	16.0	15.9	15.2	15.9	14.4	16.3

Continued

TABLE III - Continued

Sample Number	Resistance (ohms) Frequency (kilocycles second $^{-1}$)							
	10	50	100	200	300	400	500	600
				H Clay				
2	14.0	21.4	24.3	25.5	24.1	23.9	23.0	23.1
3	6.0	16.1	16.7	15.9	16.1	15.9	15.4	14.2
4	6.1	15.7	16.4	16.4	15.7	15.4	14.7	14.4
5	3.3	15.1	16.1	15.9	15.2	14.9	14.5	15.2
6	3.7	15.1	15.8	15.9	14.7	15.1	14.5	14.2
7	2.2	15.0	16.0	15.9	14.7	15.4	13.8	13.8

TABLE IV

THE DEPENDENCE OF SPECIFIC CONDUCTANCE ON CONCENTRATION OF SODIUM BENTONITE CLAY AND ELECTROLYTE SOLUTIONS

Normality	Sp. Cond. (μ mhos cm^{-1})		Normality	Sp. Cond. (μ mhos cm^{-1})		Na Bentonite		
	Na Cl	K Cl		Na Cl	K Cl	Sample Number	Cons. (gm/ml)	Sp. Cond. (μ mhos cm^{-1})
0.0005	76	—	0.06	6381	7812	2	0.01158	221
0.001	129	—	0.07	7223	9548	3	0.02162	490
0.002	249	—	0.08	8490	10676	4	0.03390	903
0.004	490	—	0.09	9376	11892	5	0.04055	1163
0.005	660	—	0.10	10591	12933	6	0.05794	1649
0.008	985	—	0.20	19185	24998	7	0.06281	1780
0.01	1215	1432	0.50	44274	57462	8	0.13438	2900
0.02	2335	2795	1.00	72053	112840			
0.03	3403	4166						
0.04	4514	5382						
0.05	5469	6718						

TABLE V

NEGATIVE DEFLECTION (VOLTS) OF HIGH FREQUENCY RESPONSE TO POTASSIUM CHLORIDE SOLUTIONS

	Frequency (megacycles second $^{-1}$)					
Normality	13	30	44	57	79	192
0.01	.0848	.0677	.0490	.0410	.0238	.0213
0.02	.0526	.0573	.0504	.0477	.0324	.0316
0.03	.0381	.0459	.0437	.0453	.0336	.0350
0.04	.0291	.0375	.0379	.0405	.0319	.0350
0.05	.0233	.0318	.0334	.0369	.0299	.0334
0.06	.0201	.0277	.0293	.0332	.0278	.0314
0.07	.0171	.0240	.0261	.0297	.0254	.0284
0.08	.0143	.0212	.0235	.0269	.0234	.0274
0.09	.0135	.0200	.0220	.0252	.0224	.0257
0.10	.0117	.0180	.0202	.0237	.0209	.0234
0.20	.0053	.0099	.0115	.0129	.0129	.0149
0.50	.0013	.0040	.0055	.0057	.0064	.0071
1.00	-.0012	.0019	.0035	.0039	.0038	.0039

R_2 = 936 ohms

TABLE VI

NEGATIVE DEFLECTION (VOLTS) OF HIGH FREQUENCY RESPONSE TO SODIUM CHLORIDE SOLUTIONS

	Frequency (megacycles $second^{-1}$)					
Normality	13	30	44	57	79	192
0.0005	.0222	.0072	.0035	.0027	.0013	.0010
0.001	.0387	.0132	.0065	.0047	.0028	.0020
0.002	.0652	.0237	.0120	.0090	.0045	.0035
0.004	.0952	.0422	.0220	.0172	.0085	.0070
0.005	.1042	.0502	.0280	.0230	.0118	.0095
0.008	.0982	.0608	.0360	.0307	.0184	.0132
0.01	.0907	.0677	.0460	.0383	.0228	.0197
0.02	.0620	.0627	.0514	.0478	.0313	.0295
0.03	.0449	.0524	.0470	.0473	.0340	.0345
0.04	.0352	.0436	.0420	.0445	.0343	.0360
0.05	.0287	.0376	.0366	.0408	.0325	.0358
0.06	.0247	.0328	.0331	.0372	.0308	.0345
0.07	.0202	.0292	.0314	.0342	.0287	.0330
0.08	.0187	.0262	.0280	.0312	.0268	.0310
0.09	.0177	.0246	.0256	.0292	.0250	.0293
0.10	.0167	.0222	.0235	.0272	.0238	.0280
0.20	.0092	.0122	.0137	.0162	.0148	.0183
0.50	.0032	.0054	.0063	.0072	.0073	.0094
1.00	.0017	.0028	.0035	.0040	.0043	.0055

R_2 = 936 ohms

TABLE VII

NEGATIVE DEFLECTION (VOLTS) OF HIGH FREQUENCY RESPONSE TO SODIUM BENTONITE

Sample Number	Frequency (megacycles second^{-1}) 13	30	44	57	79	192
2	.0694	.0387	.0250	.0213	.0125	.0113
3	.0827	.0530	.0370	.0323	.0195	.0176
4	.0790	.0588	.0445	.0405	.0260	.0238
5	.0739	.0561	.0463	.0433	.0287	.0268
6	.0669	.0541	.0465	.0455	.0325	.0314
7	.0537	.0541	.0459	.0475	.0328	.0336
8	.0446	.0464	.0415	.0485	.0355	.0378

R_2 = 936 ohms

TABLE VIII

THE DEPENDENCE OF SPECIFIC CONDUCTANCE ON CONCENTRATION OF WYOMING BENTONITE CLAYS AND ELECTROLYTE SOLUTIONS

	Specific Conductance (μ mhos cm^{-1})				
Normality	Na Cl	Ca Cl_2	Normality	Na Cl	Ca Cl_2
0.0005	76		0.02	2344	2257
0.001	129	—	0.04	4532	4280
0.002	249	—	0.06	6693	6250
0.004	490	—	0.08	8681	8117
0.005	664	623	0.10	10678	10157
0.008	985		0.50	46270	41843
0.01	1215	1172	1.00	84380	74484

Sample Number	Concentration (gm/ml)	Specific Conductance (μ mhos cm^{-1})	Concentration (gm/ml)	Specific Conductance (μ mhos cm^{-1})
	Na Clay		K Clay	
2	0.00179	69	0.00225	81
3	0.00413	104	0.00462	148
4	0.00774	181	0.00894	324
5	0.01581	386	0.01770	669
6	0.02349	622	0.02702	1059
7	0.02886	768	0.03687	1493
8	0.03936	1320	—	1728
	Li Clay		Ca Clay	
2	0.00263	48	0.00177	22
3	0.00528	88	0.00369	19
4	0.01035	164	0.00778	29
5	0.02227	383	0.01516	36
6	0.03462	663	0.02315	43
7	0.04529	929	0.03170	174
8	—	—	0.04053	139

Continued

TABLE VIII - Continued

Sample Number	Concentration (gm/ml)	Specific Conductance (μ mhos cm^{-1})	Concentration (gm/ml)	Specific Conductance (μ mhos cm^{-1})
	Ba Clay		Mg Clay	
2	0.00230	14	0.00227	30
3	0.00404	23	0.00400	43
4	0.00830	27	0.00736	43
5	0.01514	43	0.01445	59
6	0.02308	37	0.02158	82
7	0.03133	39	0.02949	88
8	0.04097	51	0.03697	99
	H Clay		Al Clay	
2	0.00176	46	0.00188	53
3	0.00405	136	0.00373	29
4	0.00974	214	0.00633	26
5	0.01809	372	0.01401	31
6	0.02457	497	0.02079	31
7	0.03222	671	0.03207	60
8	—	—	0.03690	29

TABLE IX

THE NEGATIVE DEFLECTION (VOLTS) OF HIGH FREQUENCY RESPONSE TO ELECTROLYTE SOLUTIONS AND WYOMING BENTONITE CLAYS

	Thirteen Megacycles per Second				
Sample	NaCl	$CaCl_2$	Sample Number	H Clay	Al Clay
.005N	.0963	.0916	2	.0165	.0339
.01N	.0811	.0847	3	.0420	.0172
.02N	.0540	.0577	4	.0600	.0177
.04N	.0298	.0336	5	.0773	.0246
.06N	.0205	.0237	6	.0841	.0277
.08N	.0193	.0195	7	.0825	.0396
.10N	.0165	.0164	8	___	.0398
.50N	.0043	.0035			
1.00N	.0037	.0022			

Sample Number	Na Clay	K Clay	Li Clay	Ca Clay	Ba Clay	Mg Clay
2	.0249	.0288	.0222	.0088	.0075	.0125
3	.0404	.0486	.0377	.0068	.0132	.0178
4	.0559	.0728	.0574	.0150	.0175	.0193
5	.0742	.0838	.0746	.0244	.0290	.0292
6	.0769	.0763	.0750	.0319	.0333	.0401
7	.0750	.0691	.0690	.0556	.0408	.0455
8	.0647	.0573	___	.0538	.0475	.0517

Continued

TABLE IX - Continued

Forty-four Megacycles per Second					
Sample	NaCl	$CaCl_2$	Sample Number	H Clay	Al Clay
.005N	.0275	.0265	2	.0038	.0059
.01N	.0399	.0392	3	.0093	.0030
.02N	.0439	.0438	4	.0148	.0030
.04N	.0349	.0358	5	.0235	.0056
.06N	.0270	.0281	6	.0291	.0070
.08N	.0228	.0230	7	.0346	.0102
.10N	.0190	.0196	8	———	.0115
.50N	.0060	.0062			
1.00N	.0038	.0036			

Sample Number	Na Clay	K Clay	Li Clay	Ca Clay	Ba Clay	Mg Clay
2	.0056	.0075	.0046	.0002	.0014	.0020
3	.0105	.0118	.0090	.0010	.0028	.0033
4	.0164	.0207	.0161	.0020	.0050	.0044
5	.0271	.0320	.0269	.0056	.0090	.0060
6	.0326	.0379	.0341	.0093	.0123	.0097
7	.0354	.0407	.0364	.0156	.0145	.0123
8	.0401	.0408	———	.0175	.0180	.0147

Continued

TABLE IX - Continued

Sample	NaCl	$CaCl_2$	Sample Number	H Clay	Al Clay
	Seventy-nine Megacycles per Second				
.005N	.0111	.0103	2	.0013	.0020
.01N	.0179	.0172	3	.0035	.0010
.02N	.0257	.0253	4	.0065	.0008
.04N	.0279	.0279	5	.0105	.0017
.06N	.0246	.0251	6	.0138	.0027
.08N	.0214	.0220	7	.0174	.0047
.10N	.0190	.0196	8	—	.0054
.50N	.0058	.0055			
1.00N	.0034	.0033			

Sample Number	Na Clay	K Clay	Li Clay	Ca Clay	Ba Clay	Mg Clay
2	.0025	.0025	.0024	.0006	.0010	.0010
3	.0042	.0050	.0042	.0002	.0017	.0016
4	.0072	.0085	.0076	.0012	.0029	.0024
5	.0127	.0150	.0139	.0032	.0046	.0038
6	.0172	.0202	.0191	.0052	.0062	.0057
7	.0197	.0240	.0232	.0085	.0080	.0073
8	.0242	.0250	—	.0098	.0103	.0087

Continued

TABLE IX - Continued

Sample	One hundred ninety-two Megacycles per Second NaCl	$CaCl_2$	Sample Number	H Clay	Al Clay
.005N	.0093	.0088	2	.0012	.0013
.01N	.0156	.0152	3	.0032	.0013
.02N	.0246	.0240	4	.0058	.0019
.04N	.0291	.0291	5	.0093	.0030
.06N	.0273	.0278	6	.0121	.0037
.08N	.0243	.0251	7	.0158	.0053
.10N	.0214	.0224	8	___	.0057
.50N	.0062	.0071			
1.00N	.0036	.0049			

Sample Number	Na Clay	K Clay	Li Clay	Ca Clay	Ba Clay	Mg Clay
2	.0033	.0034	.0033	.0003	.0004	.0007
3	.0053	.0046	.0047	.0009	.0009	.0010
4	.0070	.0085	.0077	.0016	.0019	.0018
5	.0124	.0150	.0139	.0035	.0036	.0032
6	.0169	.0203	.0192	.0053	.0050	.0041
7	.0193	.0243	.0234	.0077	.0067	.0055
8	.0245	.0270	___	.0094	.0085	.0069

TABLE X

CHANGE IN RESPONSE TO VARIATION IN MOISTURE OF CLAY-SAND MIXTURES

Frequency (megacycles per second)	5% Clay-95% Sand				10% Clay-90% Sand			
	Sample Number							
	17		31		35		423	
	Percent Moisture							
	0.49	0.58	0.65	1.02	1.01	1.29	0.99	1.39
13	.0584	.0800	.0541	.0983	.0427	.0572	.0323	.0510
30	.0359	.0448	.0318	.0504	.0263	.0324	.0227	.0294
44	.0249	.0305	.0226	.0344	.0179	.0228	.0155	.0203
57	.0208	.0268	.0186	.0292	.0158	.0198	.0123	.0168
79	.0125	.0169	.0115	.0188	.0097	.0130	.0082	.0113
192	.0139	.0182	.0128	.0207	.0132	.0150	.0113	.0127
	1.48	1.85	1.70	2.11	1.79	2.08	1.93	2.56
13	.1377	.1347	.1366	.1349	.1110	.1232	.1150	.1293
30	.0754	.0802	.0727	.0781	.0567	.0685	.0587	.0730
44	.0489	.0539	.0462	.0522	.0358	.0448	.0367	.0478
57	.0420	.0464	.0398	.0444	.0314	.0381	.0310	.0414
79	.0308	.0410	.0284	.0372	.0200	.0286	.0194	.0316
192	.0537	.0584	.0521	.0581	.0300	.0454	.0520	.0442
	2.73	4.36	2.93	5.28	3.08	5.03	3.92	5.86
13	.1349	.1164	.1309	.1151	.1305	.1041	.1310	.1100
30	.0848	.0810	.0788	.0797	.0771	.0765	.0785	.0785
44	.0584	.0573	.0534	.0568	.0517	.0553	.0531	.0561
57	.0529	.0522	.0476	.0519	.0460	.0510	.0473	.0514
79	.0668	.0659	.0444	.0654	.0411	.0659	.0432	.0665
192	.0601	.0581	.0569	.0578	.0580	.0589	.0585	.0594

TABLE XI

CHANGE IN RESPONSE TO VARIATION IN BUTANOL CONTENT OF CLAY-SAND MIXTURES

Frequency (megacycles per second)	5% Clay-95% Sand				10% Clay-90% Sand			
	Sample Number							
	2		21		33		42	
	Percent Moisture							
	0.47	1.51	0.47	—	0.60	1.65	0.61	1.61
13	.0045	.0292	.0123	.0349	.0158	.0327	.0243	.0383
30	.0005	.0137	.0057	.0176	.0084	.0177	.0113	.0213
44	.0019	.0113	.0033	.0119	.0044	.0137	.0079	.0138
57	.0018	.0054	.0028	.0095	.0037	.0088	.0062	.0116
79	.0031	.0041	.0007	.0068	.0012	.0067	.0030	.0080
192	.0011	.0058	.0019	.0068	.0023	.0065	.0041	.0085
	2.42	3.20	2.44	3.23	2.61	3.19	2.54	3.29
13	.0262	.0282	.0345	.0365	.0351	.0342	.0341	.0353
30	.0131	.0119	.0189	.0184	.0201	.0171	.0192	.0168
44	.0087	.0082	.0131	.0121	.0127	.0124	.0133	.0112
57	.0072	.0070	.0126	.0103	.0113	.0097	.0114	.0091
79	.0042	.0037	.0090	.0065	.0084	.0056	.0084	.0059
192	.0039	.0055	.0073	.0082	.0063	.0064	.0075	.0067
	4.07		4.21		4.66		4.57	
13	.0296		.0419		.0419		.0378	
30	.0139		.0215		.0213		.0190	
44	.0097		.0150		.0146		.0135	
57	.0075		.0128		.0120		.0107	
79	.0057		.0096		.0090		.0089	
192	.0043		.0078		.0070		.0070	

TABLE XII

CHANGE IN RESPONSE TO VARIATION IN OCTANOL CONTENT OF CLAY-SAND MIXTURES

Frequency (megacycles per second)	5% Clay-95% Sand				10% Clay-90% Sand			
	Sample Number							
	18		27		32		412	
	Percent Moisture							
	0.84	1.89	0.77	1.81	0.82	1.98	0.86	2.01
13	.0092	.0363	.0064	.0282	.0110	.0243	.0075	.0260
30	.0048	.0196	.0038	.0159	.0060	.0160	.0044	.0142
44	.0033	.0142	.0034	.0123	.0038	.0113	.0032	.0114
57	.0030	.0116	.0022	.0106	.0045	.0105	.0027	.0094
79	.0015	.0085	.0007	.0073	.0018	.0074	.0008	.0069
192	.0018	.0079	.0016	.0069	.0034	.0073	.0020	.0068
	2.75	3.52	2.51	3.28	2.80	3.55	2.87	3.56
13	.0271	.0203	.0245	.0180	.0268	.0230	.0213	.0180
30	.0118	.0080	.0109	.0068	.0126	.0101	.0109	.0075
44	.0084	.0068	.0080	.0070	.0086	.0081	.0075	.0078
57	.0070	.0088	.0062	.0068	.0074	.0083	.0056	.0071
79	.0054	.0081	.0046	.0053	.0057	.0062	.0049	.0067
192	.0042	.0134	.0051	.0066	.0056	.0082	.0046	.0070
	4.46		4.34		5.59		4.11	
13	.0298		.0272		.0327		.0258	
30	.0150		.0144		.0169		.0135	
44	.0114		.0112		.0125		.0102	
57	.0096		.0090		.0114		.0087	
79	.0076		.0070		.0079		.0069	
192	.0070		.0068		.0093		.0072	

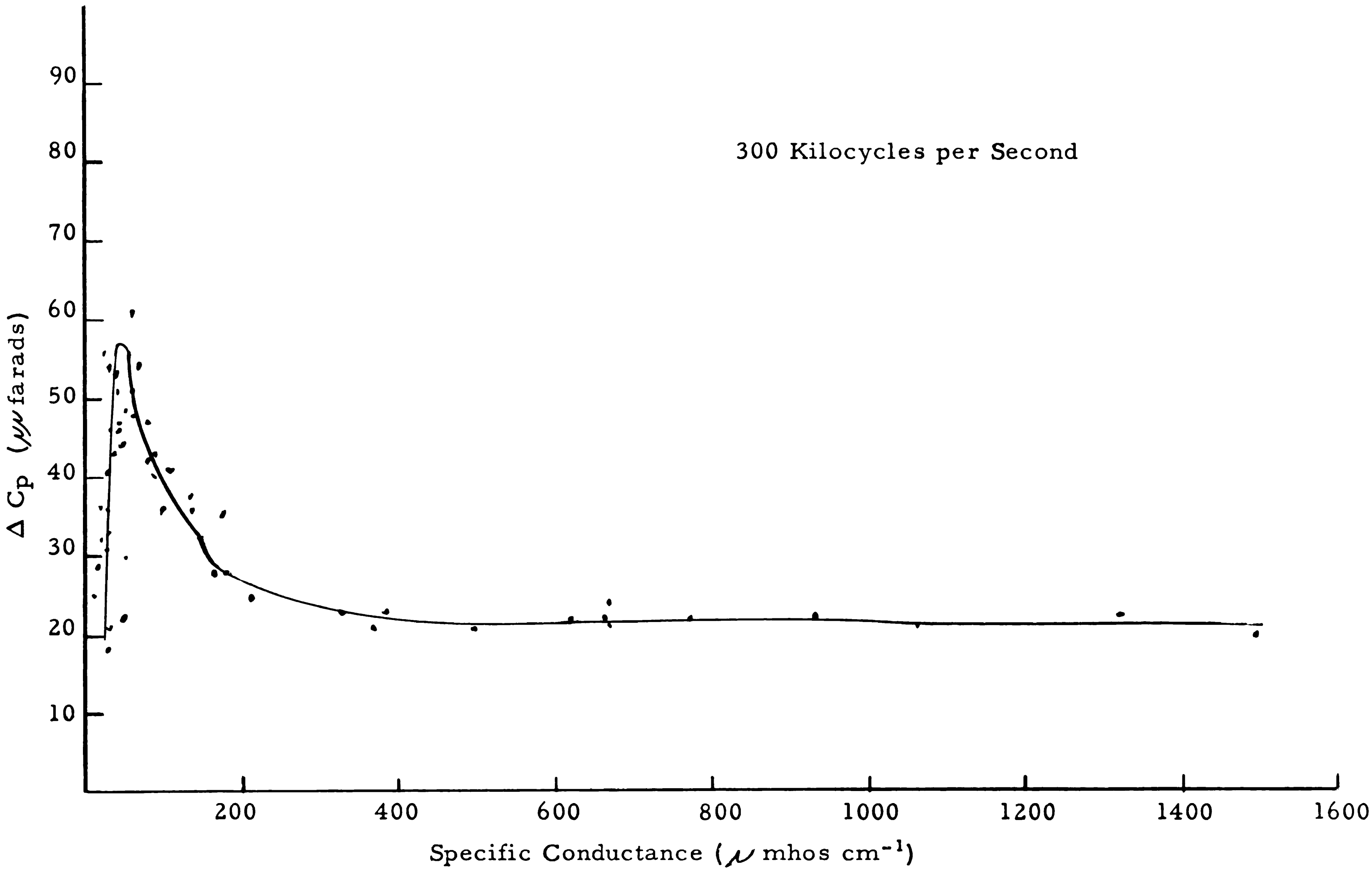

Figure 36. The relationship of the change in parallel capacitance to the specific conductance of the clay suspensions at 300 kilocycles per second.

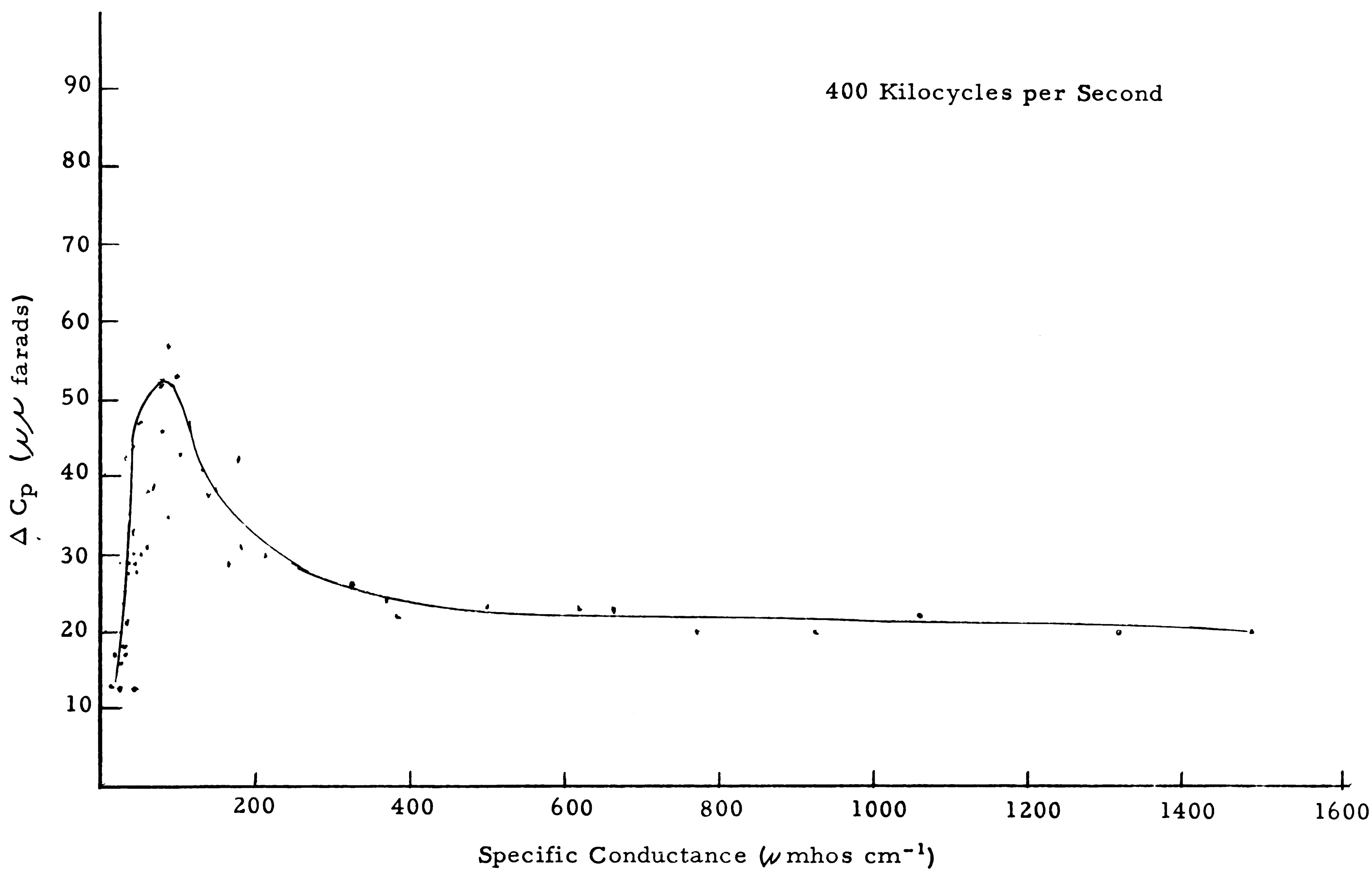

Figure 37. The relationship of the change in parallel capacitance to the specific conductance of the clay suspensions at 400 kilocycles per second.

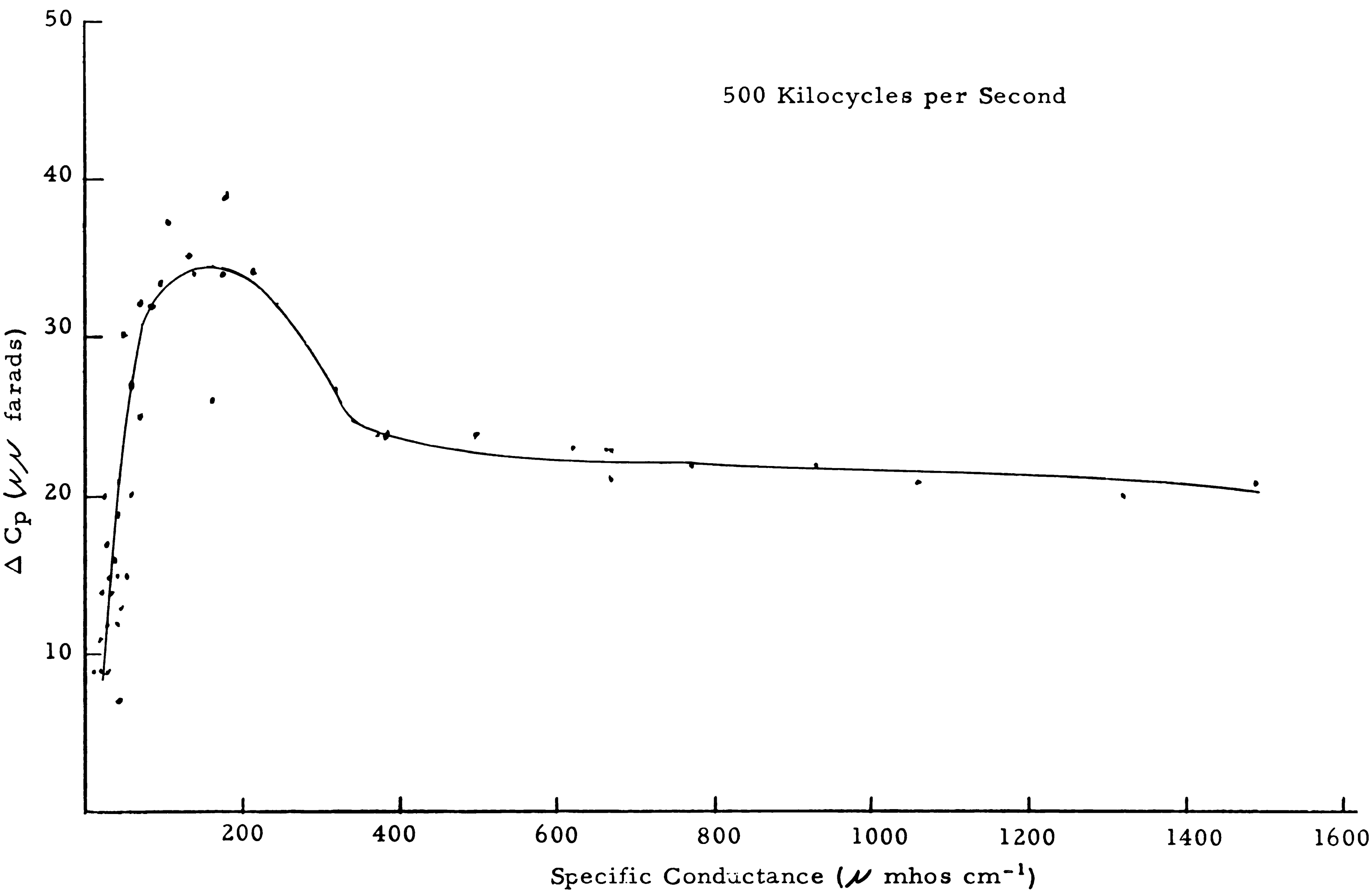

Figure 38. The relationship of the change in parallel capacitance to the specific conductance of the clay suspensions at 500 kilocycles per second.

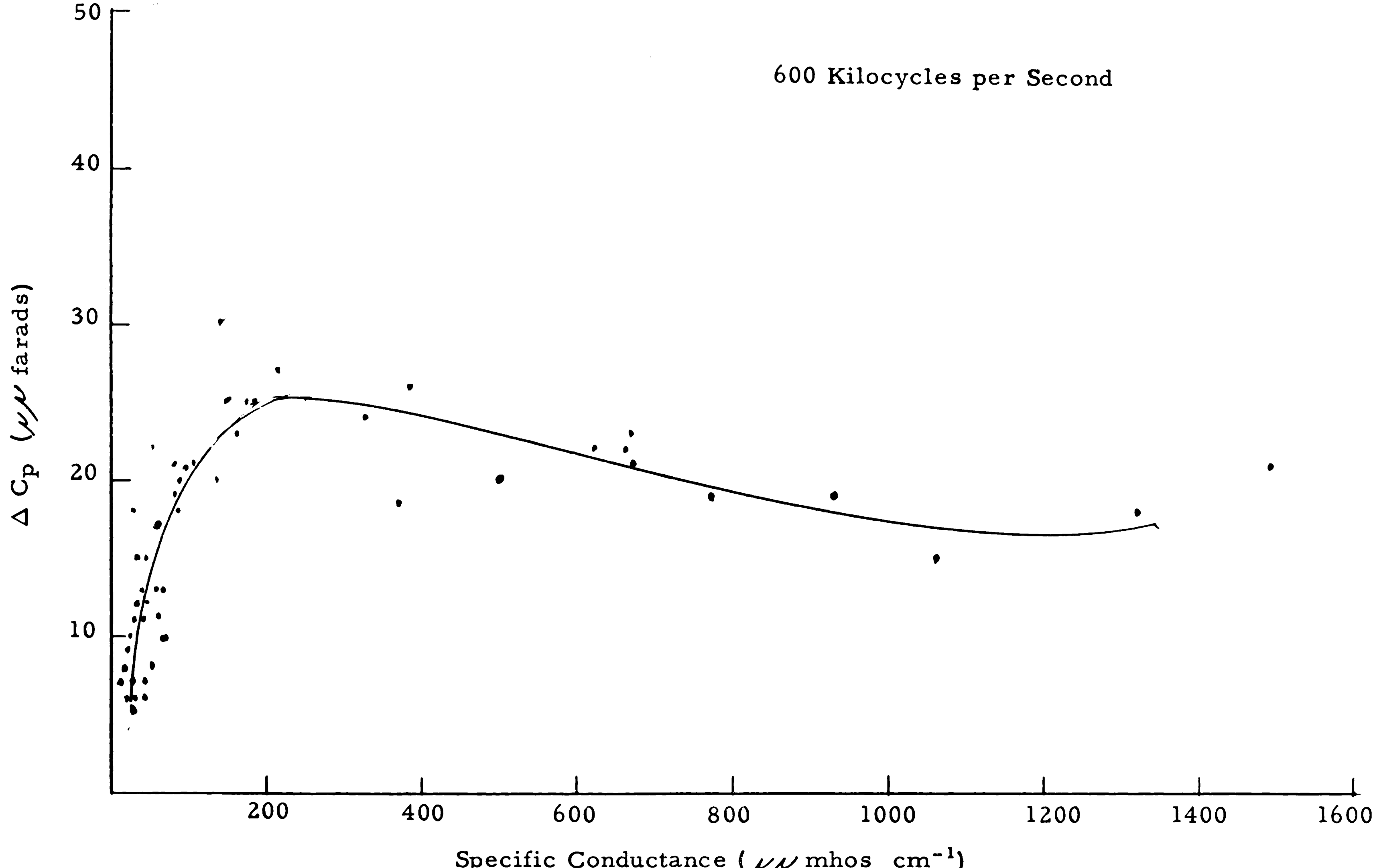

Figure 39. The relationship of the change in parallel capacitance to the specific conductance of the clay suspensions at 600 kilocycles per second.