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THE APPLICATION OF THE VERWEY-OVERBEEK  
THEORY TO THE RELATIVE SEDIMENT VOLUME  
OF KAOLIN-WATER DISPERSIONS

by

James E. Kline

A Thesis submitted to the  
Faculty of the School of Graduate  
Studies in partial fulfillment  
of the  
Degree of Master of Arts

Western Michigan University  
Kalamazoo, Michigan  
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James E. Kline

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## INTRODUCTION

This paper describes an investigation intended to:

1. observe the effect of electrolyte concentration on the stability of kaolin-water systems,
2. evaluate the relative sediment volume measurement as a tool for determining the stability of such systems,
3. assess the applicability of the Verwey-Overbeek theory of stability of lyophobic colloids for predicting the observed effects, and
4. determine if any correlation exists between the effects predicted by the theory and observed through the relative sediment volume measurement.

The relative sediment volume measurement will be shown to be dependent upon the efficiency of packing of the pigment particles, which in turn is dependent on the degree of flocculation or agglomeration of the pigment particles. Because of the relationship between relative sediment volume and degree of agglomeration, the measurement of relative sediment volume has been adopted by many workers in the area of pigment research as a valid measurement of the quality of dispersion. This paper discusses the validity of such measurements when the degree of flocculation is changed by the addition of electrolytes.

The Verwey-Overbeek theory of lyophobic colloids considers, in part, the effect of electrolytes on the stability of the dispersed system. The general effects predicted by the Verwey-Overbeek theory have been recognized for some time to be similar to the effect of electrolyte concentration on kaolin-water systems. Although absolute applicability of the Verwey-Overbeek theory has not been shown, it is gaining broad acceptance in the explanation of kaolin-water dispersion phenomena. This paper discusses some problems encountered in the calculation of the stability of kaolin-water systems using the Verwey-Overbeek theory.

## HISTORICAL BACKGROUND AND DEVELOPMENT OF THE PROBLEM

### The Relative Sediment Volume Measurement

Relative sediment volume (hereafter referred to as RSV) is the ratio of the volume occupied by the sediment to the volume of the solid particles in the sediment, and is defined and calculated as follows:<sup>14</sup>

$$RSV = \frac{V_s + V_v}{V_s} \quad (1)$$

$V_s$  = the solid volume in the sediment

$$V_s = \frac{\text{weight of pigment in the sediment}}{\text{specific gravity of the pigment}} \quad (2)$$

$V_v$  = the void volume in the sediment

$V_s + V_v$  = the total sediment volume

With RSV thus defined, it becomes obvious that if the weight of pigment in the sediment is held constant the only way to change RSV would be to change the void volume in the sediment. The void volume is directly related to the degree of flocculation in the dispersion through the efficiency of packing of the particles in the sediment.

The sediment can be obtained by almost any method



which will separate the solid phase of the dispersion from the liquid phase. Accordingly, evaporation, sedimentation or filtration are the main three means employed to obtain a sediment.

If the measurement is made by sedimentation, whether gravitational or centrifugal, the volume of the sediment can be measured directly, or the volume of supernate can be measured. By subtracting the volume of supernate from the total volume of water in the sample, one can obtain a value for the void volume in the sediment. Equation (1) can then be used to calculate RSV. These methods are subject to error due to experimental difficulties in determining accurately the weight of pigment in the sample, and the volume of the sediment or the volume of the supernate.

With the filtration technique, the sediment volume must be calculated by difference using the volume of the filtrate as the volume of the supernate was used in the preceding example. Further errors are introduced through the difficulty encountered in determining the endpoint of the filtration process.

The evaporation technique allows one to measure the weight of pigment in the sediment directly, and eliminates the errors due to calculating this value.

However, measuring the total sediment volume is much more difficult than in the other two methods.

Hagemeyer<sup>3</sup> used both a sedimentation and a filtration technique, and showed that the results obtained by the two methods on the same dispersed system are not comparable. The data reported by Hagemeyer<sup>3</sup> can be further interpreted to show poor correlation between duplicate runs, however it should be noted that some of the data in his paper were received from different investigators and therefore could be subject to variations in the techniques employed. One would expect poor correlation between the evaporation method and either of the other two techniques since during evaporation of the water the electrolyte concentration would be changing and therefore the degree of flocculation of the system would be changing. Kandilarov<sup>5-9</sup> used the evaporation technique in his investigations, but because of the changing electrolyte concentration, it is impossible to determine the electrolyte concentration at the moment the sediment is formed. Accordingly, the results of this technique cannot be compared with the other two techniques.

Although data of the above three authors cannot be compared directly, they all indicate that the addition

of an electrolyte to a pigment dispersion should cause the RSV to be low in a system which would normally be considered stable, and high in systems considered to be unstable or flocculated. Robinson<sup>13,14</sup> reported the effect of various forms and intensities of mixing on the RSV of pigment dispersions, and concluded that a greater degree of flocculation will lead to an increased RSV. Hagemeyer<sup>2,3</sup> reported on the effect of particle shape on RSV and concluded that although the shape of the particles is important, the RSV is also affected by the amount and type of chemical dispersant present. Kandilarov<sup>5-9</sup> presented considerable evidence that the RSV decreases initially as the electrolyte is added, passes through a minimum and then increases with continued addition of electrolyte.

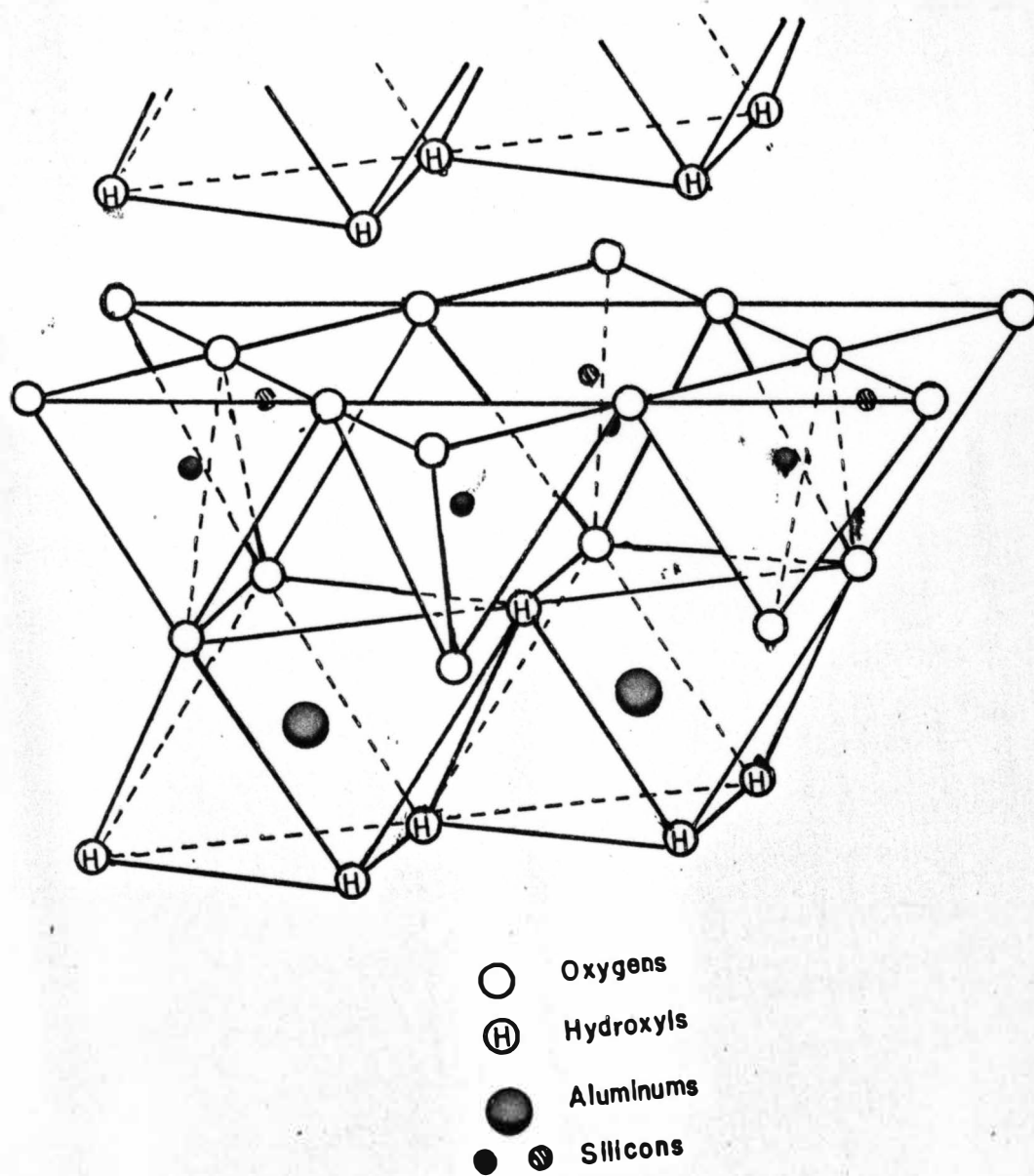
In spite of the experimental errors involved in making the measurement, there is sufficient evidence that the RSV measurement is dependent on the degree of flocculation and should be examined closely for the validity of its use in measuring the quality of the dispersion.

## Kaolin as a Colloidal Material

### Kaolin mineralogy

The mineral kaolin exists naturally as hexagonal plates of variable dimensions composed of several layers of the kaolinite crystal structure which are hydrogen bonded between the octahedral aluminum oxide layer and the silica sheets as indicated in Figure 1.<sup>1</sup> For most uses of kaolin it is desirable to have the particles reduced to a fairly small and uniform particle size through wet or dry milling, which reduces the booklets to individual plates and also reduces the size of the plates. The plate shaped particles can be fractured parallel or perpendicular to the silica and alumina sheets. Fracture in the parallel plane would probably occur where the silica sheet is hydrogen bonded to the octahedral aluminum oxide layer. Fracture in the perpendicular direction would break primary bonds and create some degree of unsaturation on the edges of the resultant particles.

Fig.1 The Structure of Kaolinite



### Origin of the electrical charge

There are basically three methods whereby the kaolin particles can acquire a charge: 1. substitution within the crystalline lattice, 2. creation of active sites due to unsaturation from broken bonds, and 3. adsorption of ions onto the surface in nonactive areas. The first method can be neglected since the extent of atom substitution in the kaolinite structure is very small.

The second method of charge acquisition can be seen to be quite likely if cleavage of the particles occurs perpendicular to the basal plane as described in the previous section. There is evidence<sup>12</sup> that kaolin particles do cleave perpendicular to the basal plane creating a positive charge on the edges of the plates. When the kaolin particles are placed in water, however, the positive edges would tend to become neutralized through hydration. If negative ions were added to the system, they would be attracted to the positive edges and would decrease or completely neutralize the positive charge. For these reasons, it is felt that addition of sufficient electrolyte to the system will negate the positive charge and cause the edges to behave as if they were neutral or negatively

charged.

The surfaces of the particles tend to acquire a charge through the third method. If the basal plane cleavage does occur between the silica and gibbsite layers destroying only hydrogen bonding, then the surfaces would have either hydroxyl groups or oxygen atoms exposed. A surface of this type would be an excellent site for the adsorption of certain negative ions with the aid of hydrogen bonding.

#### The electrical charge and colloidal stability

The total charge distribution on the particles in the absence of other ions would result in plates with positively charged edges and at least slightly negative surfaces. Such a situation should lead to agglomeration or flocculation of the particles in an edge to face configuration.<sup>12</sup> Such flocculation should be characterized by high plastic flow displaying a high yield value and also should produce a high value for the RSV measurement.

As electrolyte is introduced to the suspension, electrical double layers will build on the surface and edge of the particles. Although the double layers may be of opposite charge initially, it is believed<sup>12</sup>

that the total effect becomes the same as if there is only one layer which is negative at the surface of the particle. The stability of particles having this type of charge configuration should be subject to the Verwey-Overbeek theory, which is discussed in the next section.

### The Verwey-Overbeek Theory

The Verwey-Overbeek theory of stability of lyophobic colloids covers many facets of the numerous interactions which can occur between solid particles suspended in a fluid medium. The theory relates these interactions, generally in the form of attractive and repulsive potential energies, to the many contributing characteristics of the particles and the suspending fluid. The theory was developed for three different particle shapes- plates, rods and spheres. For each particle shape, different equations have been derived for the potential energy between the particles. Because of the shape of the kaolin particle, this discussion will consider only the equations for plate shaped particles, and the fluid medium considered will be varying concentrations of electrolytes in water.

Considering van der Waals-London attractive forces to apply, Verwey and Overbeek<sup>15</sup> have developed the



following relationship for the potential energy associated with the attraction between the plates ( $V_a$ ):

$$V_a = - \frac{A}{48\pi} \left[ \frac{1}{d^2} + \frac{1}{(d+\delta)^2} - \frac{2}{(d+\delta/2)^2} \right] \quad (3)$$

where  $d$  = half the distance of separation between the plates, cm,

$\delta$  = the thickness of the plates, cm,

$A$  = a constant for the given chemical composition of the particles, ergs.

Verwey and Overbeek have further shown that equation (3) can be simplified in the following manner depending on the relative sizes of  $d$  and  $\delta$ :

$$\text{if } d \gg \delta \quad V_a = - \frac{\delta^2 A}{32\pi d^4} \quad (4)$$

$$\text{if } d < \delta \quad V_a = - \frac{A(1/d^2 - 7/\delta^2)}{48\pi} \quad (5)$$

$$\text{if } d \ll \delta \quad V_a = - \frac{A}{48\pi d^2} \quad (6)$$

It will be shown later that interaction between the particles in consideration occurs at a distance of separation which would evaluate  $d$  at about  $1 \times 10^{-7}$  cm as the lowest possible value and about  $2 \times 10^{-6}$  cm as the highest possible value. The average particle thickness  $\delta$  is estimated by Grim<sup>1</sup> to be between  $2 \times 10^{-4}$  cm and  $5 \times 10^{-6}$  cm. Comparison of these values shows  $d$

to be less than 6 in all cases and allows the use of equation (6) in calculating the attraction potential energy. It can therefore be seen from equation (6) that the attraction potential is inversely proportional to the square of the distance of separation between the particles and is independent of the electrolyte concentration in the intermicellar solution or the charge on the particle.

The repulsion potential energy, however, is dependent on the electrolyte concentration in the intermicellar solution. The expression for the repulsion potential energy ( $V_r$ ) as developed by Verwey and Overbeek<sup>15</sup> is shown in equation (7).

$$V_r = \frac{32nkT}{x} (1 - \tanh xd) x^2 \quad (7)$$

where  $n$  = the number of ions of opposite charge to the particle contained in one cubic centimeter of the intermicellar solution,

$k$  = the Boltzmann constant,

$T$  = the absolute temperature,

$d$  = half the distance of separation between the plates, cm.,

$x$  = a parameter related to the reciprocal of the effective thickness of the electrical double layer,  $\text{cm.}^{-1}$ , which can be defined as;

$$\kappa = \sqrt{\frac{8\pi n \epsilon^2 v^2}{DkT}} \quad (8)$$

where  $\epsilon$  = the charge on the electron, absolute e.s.u.,

$v$  = the valence of the counterions,

$D$  = the dielectric constant of water

$$\text{and } \gamma = \frac{-1 + e^{z/2}}{+1 + e^{z/2}} \quad (9)$$

where  $z$  is the electric surface potential and can be

$$\text{expressed as } z = \frac{v \epsilon \psi_0}{300kT} \quad (10)$$

and  $\psi_0$  = the potential existing between the surface of the particle and the intermicellar solution in volts.

It can be seen that the terms included in the calculation of the repulsion potential are readily available with the exception of the electric surface potential,  $\gamma$ . Difficulties in evaluating this parameter are due to an inability to measure accurately the potential existing between the surface of the particle and the intermicellar solution,  $\psi_0$ . However, this measurement can be bypassed if the surface charge density ( $\sigma$ ) is known. Verwey and Overbeek<sup>13</sup> have developed the following equation for the evaluation of  $\sigma$ :

$$\sigma = \sqrt{\frac{2nDkT}{\pi}} \cdot \sinh (z/2) \quad (11)$$

$\sigma$  can also be calculated from the following expression;

$$\sigma = \frac{N\epsilon}{a'}(M) \quad (12)$$

where  $N$  = Avogadro's number,  $6.02 \times 10^{20}$  ions/millimole

$a'$  = specific surface area of the particles  $\text{cm}^2/\text{g}.$ ,

and  $M$  = the milliequivalents of anion adsorbed per gram of solid material.

Through the use of equation (12)  $\sigma$  can be calculated from available data, in most cases. With  $\sigma$  thus determined,  $\gamma$  can be calculated through introduction of the parameter ( $p$ ).

$$\text{where } p = \sigma \sqrt{\pi / 2DkTn} \quad (13)$$

Through the use of the parameter  $p$ , equation (11) can be rewritten as follows:

$$z/2 = \sinh^{-1} p \quad (14)$$

$$\text{however, } \sinh^{-1} p = \ln(p + \sqrt{p^2 + 1}) \quad (15)$$

$$\text{thus, } z/2 = \ln(p + \sqrt{p^2 + 1}) \quad (16)$$

$$\text{and, } \gamma = \frac{p + \sqrt{p^2 + 1} - 1}{p + \sqrt{p^2 + 1} + 1} \quad (17)$$

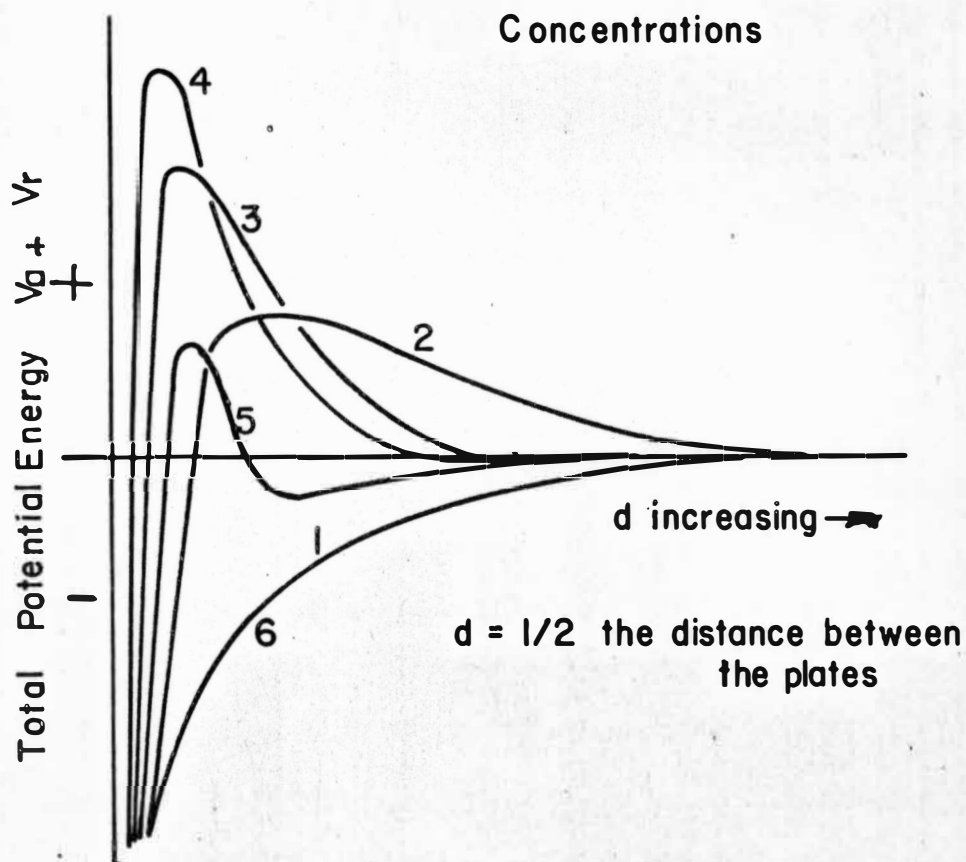
With  $\gamma$  evaluated, the potential energy of repulsion can be calculated, using equation (7). (See Appendix I for a sample solution to these equations.)

The total potential energy between the two plates is the sum of the attractive and repulsive energies.

Since the attraction potential is always negative and the repulsion potential is always positive, a negative value for the total potential energy would indicate a system in which the plates would be drawn together, and a positive value would indicate a system where the plates would be repelled.

The normal application of these values is to plot curves showing the change in the potential energy between the plates as the distance between the plates is decreased as shown in Figure 2. If the potential energy is negative at any distance of separation, the particles will be drawn close together until they come into contact or until the curve passes above the zero potential line indicating repulsion between the plates. If the potential energy is positive, the plates will be held apart unless some outside force is introduced which can overcome the potential energy of repulsion and bring the particles into contact. Therefore, any curve which remains negative for all distances of separation would indicate an unstable system which will flocculate spontaneously. Accordingly, any curve which exhibits a maximum on the positive side of the zero potential line would indicate a system which is stable. Furthermore, if one system is represented by

Fig. 2 Potential Energy Curves at Varying Electrolyte Concentrations



a curve showing a higher maximum than another system, the system with the curve having the highest maximum would be considered to be the most stable.

Verwey and Overbeek<sup>15</sup> have shown the effect of an electrolyte on the stability of a dispersion, a synopsis of which is found in Figure 2 and the following discussion.

Figure 2 can be used to represent the findings of Verwey and Overbeek in the following manner: Curve 1 represents a system containing little or no electrolyte. The charge density, and accordingly the repulsion potential, would therefore be small and the shape of the curve indicates a system which is very unstable and would flocculate spontaneously. Curves 2, 3, and 4 represent increasing concentrations of electrolyte and show the stability of the dispersions to be increasing. In curve 5 there is a decrease in the height of the maximum indicating a decrease in stability. Curve 5 is a special case showing both a maximum and a minimum. Theoretically, the plates would be drawn into the minimum "well" and would remain there until disturbed by an outside force. Note in curves 2 through 4 that the position of the maximum is shifting closer to the potential energy axis, i.e., the minimum distance allowed between the particles prior to flocculation is

decreasing with increasing electrolyte concentration. Curve 6 roughly coincides with curve 1 and represents electrolyte concentrations greater than found in curve 5. Curve 6 represents what is referred to as an over-dispersed system and is one which would lead directly to flocculation. The Verwey-Overbeek theory therefore predicts that as the electrolyte concentration is increased, the system should become more stable, pass through a system of maximum stability and then become flocculated again due to the addition of too much electrolyte.

#### Development of the Problem

The preceding sections show that the effect of electrolyte concentration predicted by the Verwey-Overbeek theory is in agreement with the observed effect of electrolytes as measured by the relative sediment volume. The RSV measurement is also shown to be subject to many possible sources of error, but is still believed to be worthy of closer examination.

Holtzman<sup>4</sup> demonstrated how the potential energy functions could be solved for kaolin-water systems, and evaluated the necessary constants. Holtzman<sup>4</sup> also claimed complete applicability of the Verwey-Overbeek



theory to kaolin-water systems, however in his work he did not take into account the possibility of plates with positive edges and negative faces. Furthermore, Holtzman<sup>4</sup> worked with very low solids systems (about 5% solids) and did not test the systems he prepared for stability but relied on published data which was based on higher solids systems. It is therefore felt that further investigation into the applicability of the Verwey-Overbeek theory is not only desirable but necessary in view of its growing acceptance as a valid tool for kaolin-water systems.

## EXPERIMENTAL SECTION

### The Purification of Water

In order to insure against extraneous ions entering into the systems to be analyzed, it was decided to produce and use water of as high purity as possible. Therefore either distilled or deionized water of approximately 2,000 ohms/cm specific resistance was further purified to around 1,000,000 ohms/cm specific resistance by one additional pass through a bed of mixed resin. (Rexyn 300)

### The Purification of Clay

If the amount of electrolyte in contact with the clay is to be controlled and measured, it is necessary to produce clay samples which are as free as possible from adsorbed ions.

In order to have a uniform starting material for all experiments a commercially available predispersed clay in the 80% less than 2 micron size range was mechanically dispersed and deionized according to the following outline.

1. A 3,600 g charge of air dry clay was mixed at 75% solids in a laboratory size sigma blade kneader.

2. The clay dispersion was diluted to either 70% or 60% solids for removal from the kneader.

3. The clay dispersion then was mixed with one pound of Rexyn 203 exchange resin in the hydroxyl form, which constituted about a two fold excess of resin.

4. After equilibration, the resin was separated from the clay through vacuum filtration using a stainless steel wire screen of about 100 mesh which satisfactorily retained the resin.

5. The clay dispersion was next mixed with one pound of Rexyn 101 exchange resin in the acid form and allowed to equilibrate.

6. The resin was again removed from the clay by the method outlined above, or by pressure filtration using a Barroid pressure filter under 20 or 100 pounds of pressure.

The above resins were regenerated by the method described by Holtzman<sup>4</sup> and rinsed separately until the specific resistance of the eluant exceeded 200,000 ohm-cm.

#### Preparation of the Sample for Testing

Since Robinson<sup>13</sup> showed the RSV to be dependent on

the amount and intensity of agitation, several techniques were tried in an attempt to control this variable.

Simple stirring of the samples with a stirring rod gave too great a variability. The first satisfactory procedure was to use a vibratory mixer. Although the vibratory mixer reduced the variability of duplicate runs at a given solids level, variations were still observed in the minimum RSV obtainable at different percent solids levels. Small ball mill jars were next tried, but the results were the same as for the vibratory mixer. The data reported in this paper, however, were obtained by the first two techniques.

The general procedure was as follows;

1. The desired amount of deionized clay was weighed into the mixing vessel.
2. The desired amount of dispersing electrolyte was added from an aliquot of a standard solution.
3. The necessary amount of dilution water for the desired solids level was then added.
4. The samples mixed with stirring rods or the vibratory mixer were mixed until smooth. The ball mill jars were run for one hour to insure adequate and equal treatment.

### Method of Determining RSV

All data reported in this paper were obtained through centrifugal sedimentation in an International centrifuge model no. 9904E, at 2,000 rpm for 45 minutes with the center of gravity of the samples at about 6 in. from the center. The sediment volume was determined by difference after measuring the volume of supernate. The void volume was obtained by subtracting the volume of the supernate from the calculated total volume of water in the sample. By knowing the percent solids of the starting sample and the weight of material placed in the centrifuge, the weight of pigment in the sample can be calculated. The RSV is then determined by the use of equation (1).

### Viscosity Measurement

The viscosities of the dispersions were measured on the Brookfield viscometer model RVF at the 100 rpm speed, and were converted to centipoise according to the chart supplied with the instrument.

Rheograms were prepared on the Hercules Hi-Shear Viscometer using the A bob.

## Measurement of Cation Concentration

In the application of the Verwey-Overbeek formula the value required is the intermicellar concentration of the cation, which was measured in the supernate decanted from the sediment during determination of RSV. The sodium ion concentration was determined potentiometrically using the Beckman sodium ion electrode model no. 39278 and a Beckman sodium ion electrode model no. 1019. The hydrogen ion concentration was calculated from pH measurements and added to the sodium ion concentration in systems whose pH was below 4.0.

## pH Measurement

The pH of both the clay dispersion and the supernate after centrifuging were measured on a Beckman Zeromatic pH meter model no. 96, a fiber junction saturated calomel reference electrode type 1019 and a glass electrode type 42. Standardization was accomplished by using standard buffer solutions of pH either 6.86, 4.00 or 10.00 depending on which was closest to the pH value of the solution being measured. Although the solutions measured contained sodium ions, the concentration was low enough that a correction of the read pH values was not necessary.

## Determination of Pyrophosphate on the Deionized Clay

The deionized clay was analyzed by an emission spectrographic technique to determine the residual pyrophosphate on the clay after deionization. The samples analyzed were prepared by adding 0.1, 0.3, 0.6 and 1.0% tetrasodium pyrophosphate based on the weight of the clay to three separate samples of the deionized clay. The clay samples were ball milled, dried and the analysis run on the dried samples. All spectrograms were prepared and measured using the following equipment:

1. A 220 V. DC arc source with 45 sec exposures,
2. a step sector which employed a rotating disc with openings of 180, 90, 45, 22.5, 11.25, and 5.625 degrees,
3. a Hilger medium quartz spectrograph,
4. SA-3 photographic plates,
5. D-19 developer in a rocking tray bath with 2½ minutes developing time,
6. a Hilger Microphotometer (slit opening at 10 and slit height at 7 mm).

Three plates were prepared, each containing step sector exposures of the four clay samples described earlier. The analysis was based on the silicon line at 2528.5 Å as an internal standard and the phosphorus line at 2535.7 Å.

## PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

### RSV and Viscosity of the Dispersions

The RSV data shown in Table I and Figures 3 through 10, show the RSV to behave as expected. The RSV is high for systems containing no dispersant, low for moderate amounts of dispersant and increasing as more dispersant is added. The data therefore agrees with the known fact that either too little or too much dispersant will lead to flocculated systems, while at some intermediate level of addition there will be obtained a system of a low degree of flocculation generally referred to as the optimum degree of dispersion for the system. Figures 3, 4, 7 and 8 show a variation between duplicate runs, which can best be explained by the fact that the duplicate runs were performed on different starting batches of clay, as shown in Table I. The duplicate runs at 30% solids were run on the same starting batch of clay and are shown in Figures 5 and 9 to be in very good agreement.

The type and intensity of mechanical agitation did cause some variation in the RSV, but did not lead to



Table I. Summary of experimental data.

% solids	deionized clay batch	% NaOH	pH	Na <sup>+</sup> conc. <sup>a</sup>	OH <sup>-</sup> ads. <sup>b</sup>	RSV
10	1	0.00	2.9	1.10E+18 <sup>c</sup>	0.0017	3.06
10	1	0.10	4.5	1.25E+18	0.015	3.33
10	1	0.20	6.4	1.57E+18	0.040	2.29
10	1	0.30	7.8	2.50E+18	0.065	2.04
10	1	0.40	9.6	3.60E+18	0.090	2.04
10	1	0.60	11.2	6.60E+18	0.126	2.04
10	1	0.80	11.5	8.50E+18	0.163	2.56
10	1	1.20	11.8	1.50E+19	0.236	2.72
10	1	1.60	12.0	1.80E+19	0.300	2.72
10	1	2.00	12.1	2.50E+19	0.380	3.06
10	2	0.00	3.6	- - - -	- - -	4.08
10	2	0.10	6.35	- - - -	- - -	3.32
10	2	0.20	7.8	1.55E+18	0.060	2.55
10	2	0.30	9.3	2.50E+18	0.075	2.55
10	2	0.40	10.4	3.50E+18	0.098	2.55
10	2	0.50	10.9	4.20E+18	0.113	2.55
10	2	0.60	11.3	6.00E+18	0.132	2.29
10	2	0.70	11.55	7.20E+18	0.144	2.55
10	2	0.80	11.65	7.80E+18	0.159	2.55
10	2	1.20	12.0	1.30E+19	0.210	2.60
10	2	1.60	12.1	1.85E+19	0.289	2.60
10	2	2.00	12.2	2.50E+19	0.350	2.80

---

a. sodium ion concentration in ions/cc.

b. adsorption in meq/g, calculated by pH method (p. 54), and including 0.0018 meq/g of pyrophosphate (p.59).

c. This notation will be used for all values in this column and is defined as follows: 1.10E+18 =  $1.10 \times 10^{18}$

Table I (cont.)

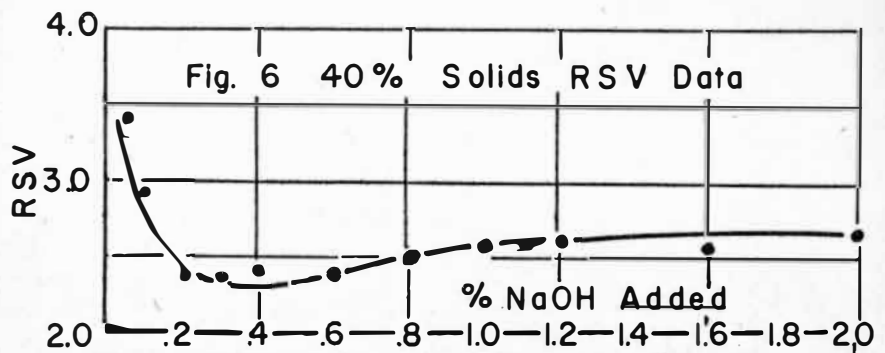
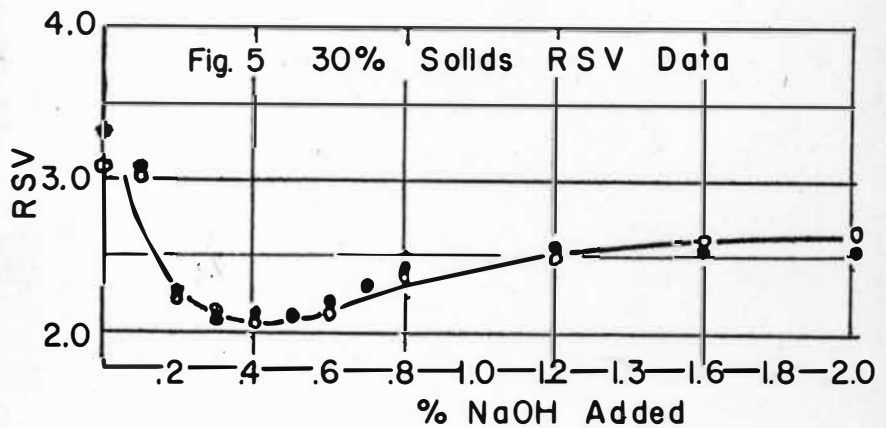
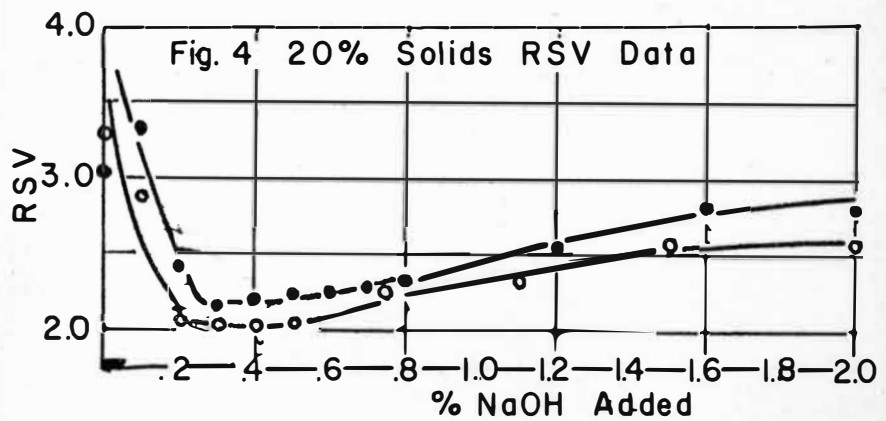
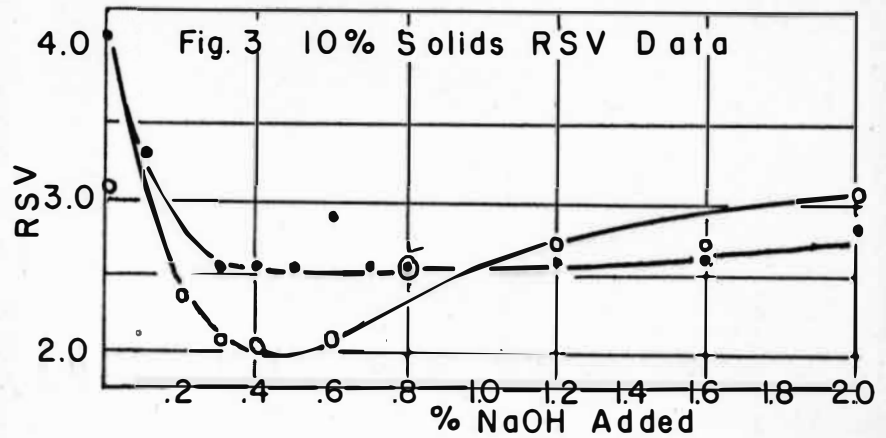
% solids	deionized clay batch	% NaOH	pH	Na <sup>+</sup> conc. <sup>a</sup>	OH <sup>-</sup> ads. <sup>b</sup>	RSV
20	1	0.00	3.3	7.80E+17	0.0017	3.28
20	1	0.10	6.1	1.50E+18	0.0237	2.87
20	1	0.20	7.1	3.20E+18	0.060	2.04
20	1	0.30	8.5	5.9E+18	0.075	2.04
20	1	0.40	10.6	9.1E+18	0.098	2.04
20	1	0.50	11.2	1.4E+19	0.114	2.04
20	1	0.00	3.3	7.8E+17	0.0017	3.2
20	1	0.40	10.5	9.6E+18	0.099	2.04
20	1	0.75	11.7	2.5E+19	0.168	2.30
20	1	1.00	11.9	3.3E+19	0.218	2.30
20	1	1.50	12.0	5.1E+19	0.335	2.55
20	1	2.00	12.2	6.3E+19	0.436	2.55
20	2	0.00	3.4	7.6E+17	0.0017	3.57
20	2	0.10	6.35	1.0E+18	0.025	3.31
20	2	0.20	7.6	2.4E+18	0.050	2.42
20	2	0.30	9.1	4.6E+18	0.074	2.13
20	2	0.40	10.3	6.6E+18	0.099	2.18
20	2	0.50	11.0	9.0E+18	0.126	2.24
20	2	0.60	11.4	1.1E+19	0.140	2.26
20	2	0.70	11.6	1.3E+19	0.159	2.28
20	2	0.80	11.75	1.6E+19	0.178	2.31
20	2	1.20	12.0	2.6E+19	0.260	2.54
20	2	1.60	12.15	3.3E+19	0.344	2.80
20	2	2.00	12.2	3.6E+19	0.436	2.80

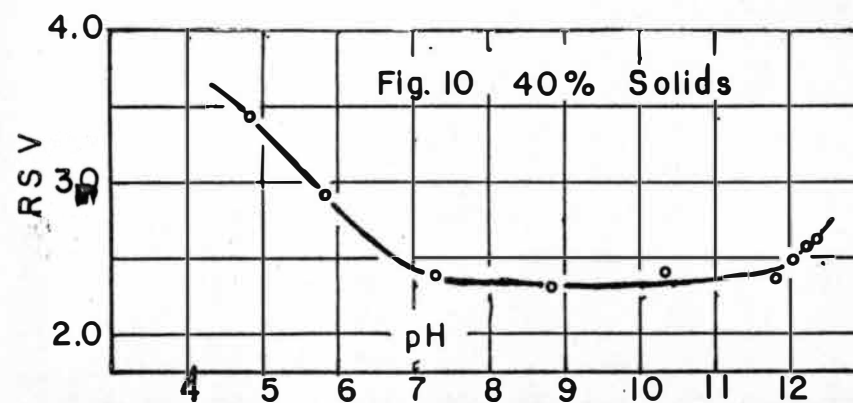
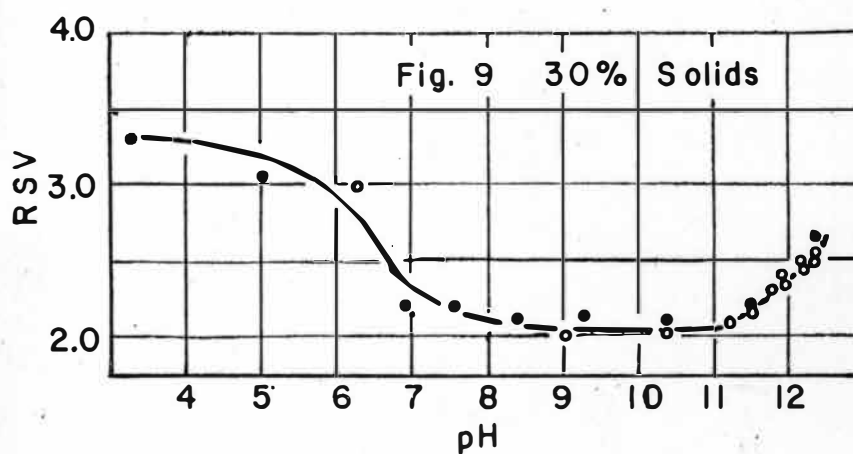
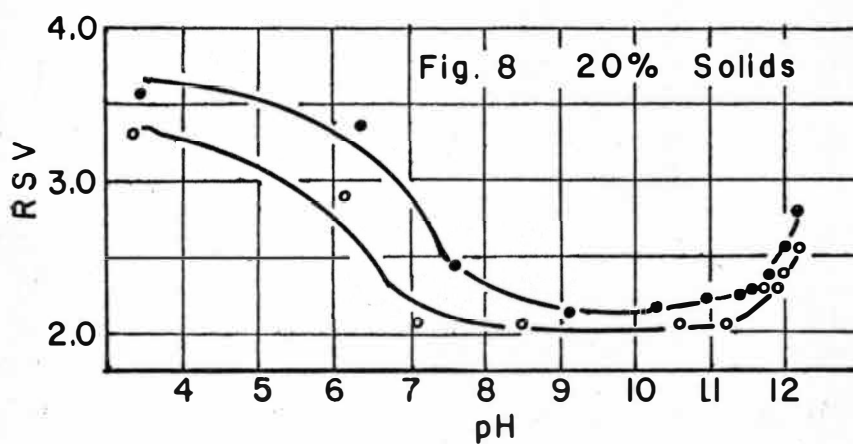
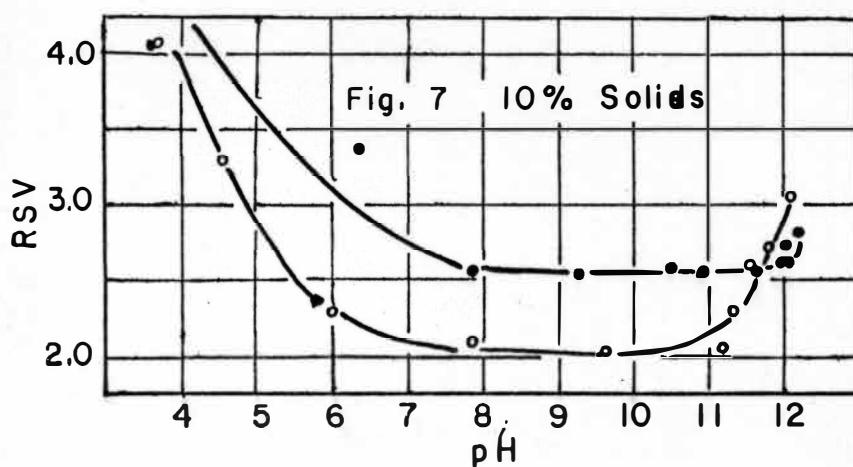
Table I (cont.)

% solids	deionized clay batch	% NaOH	pH	Na <sup>+</sup> conc. <sup>a</sup>	OH <sup>-</sup> ads. <sup>b</sup>	RSV
30	2	0.00	2.7	1.2E+18	0.0017	3.03
30	2	0.00	2.7	1.5E+18	0.0017	3.06
30	2	0.10	5.0	2.5E+18	0.0217	3.06
30	2	0.20	6.9	5.3E+18	0.047	2.20
30	2	0.30	8.4	1.1E+19	0.073	2.12
30	2	0.40	10.4	1.5E+19	0.096	2.12
30	2	0.40	9.3	1.3E+19	0.097	2.12
30	2	0.60	11.5	2.5E+19	0.139	2.12
30	2	0.80	12.0	3.8E+19	0.197	2.38
30	2	1.20	12.2	6.0E+19	0.297	2.46
30	2	1.60	12.25	8.5E+19	0.397	2.55
30	2	2.00	12.3	1.1E+20	0.497	2.64
30	2	0.00	3.3	7.2E+17	0.0017	3.30
30	2	0.10	6.3	2.2E+18	0.026	3.00
30	2	0.20	7.6	5.7E+18	0.051	2.2
30	2	0.30	9.0	1.0E+19	0.076	2.05
30	2	0.40	10.3	1.4E+19	0.101	2.05
30	2	0.50	11.2	2.0E+19	0.117	2.1
30	2	0.60	11.5	2.6E+19	0.143	2.2
30	2	0.70	11.75	2.7E+19	0.162	2.3
30	2	0.80	11.9	3.3E+19	0.181	2.4
30	2	1.20	12.15	5.2E+19	0.266	2.5
30	2	1.60	12.25	6.3E+19	0.356	2.5
30	2	2.00	12.25	7.4E+19	0.456	2.5

Table I (cont.)

% solids	deionized clay batch	% NaOH	pH	Na <sup>+</sup> conc. <sup>a</sup>	OH <sup>-</sup> ads. <sup>b</sup>	RSV
40	2	0.00	2.9	1.6E+18	0.0017	3.37
40	2	0.05	4.8	2.4E+18	0.0117	3.42
40	2	0.10	5.8	3.0E+18	0.025	2.91
40	2	0.20	7.3	8.4E+18	0.050	2.36
40	2	0.30	8.8	1.6E+19	0.075	2.36
40	2	0.40	10.3	2.5E+19	0.100	2.42
40	2	0.60	11.8	4.2E+19	0.140	2.36
40	2	0.80	12.0	5.9E+19	0.185	2.50
40	2	1.00	12.2	7.8E+19	0.228	2.57
40	2	1.20	12.3	9.6E+19	0.270	2.60
40	2	1.60	12.3	1.3E+20	0.37	2.55
40	2	2.00	12.3	1.5E+20	0.47	2.65





systematic variations. All samples were mechanically dispersed with the vibratory mixer except the 10% solids samples with clay batch no. 1, which were mixed with a stirring rod.

The viscosity data shown in Table II and Figure 11 have been included since viscosity is the most common means of measuring the degree of flocculation. Comparison of the RSV and viscosity data again confirms the use of RSV to measure dispersion stability in that the general shapes of the two curves are similar. However, it should be noted that the RSV data does not show as sharp a minimum as does the viscosity data. Accordingly, one must conclude that the viscosity measurement is a more sensitive gauge of the stability of the dispersion, except at low solids levels where neither measurement shows too high a degree of sensitivity.

Interpretation of the rheograms in Figures 12 and 13 shows both the 0.00% NaOH and 2.00% NaOH samples to be pseudoplastic, indicating that the systems are at least partially flocculated. Since the 0.00% NaOH samples show higher values for the yield point in both Figures than do the 2.00% NaOH samples, one must conclude that the 0.00% NaOH samples are more highly flocculated than the 2.00% NaOH samples. The higher degree of

Table II. Brookfield viscosity data

20% solids		30% solids	
% NaOH added	viscosity*	% NaOH added	viscosity*
0.0	290	0.0	1800
0.1	18.0	0.1	22
0.2	15.0	0.2	18.0
0.3	15.0	0.3	16.0
0.4	14.0	0.4	16.5
0.5	14.0	0.5	-
0.6	14.0	0.6	17.0
0.7	14.5	0.7	-
0.8	14.5	0.8	19.0
0.9	14.5	0.9	-
1.0	14.5	1.0	22
1.2	15.5	1.2	28
1.4	16.0	1.4	34
1.6	20.0	1.6	38
1.8	21	1.8	44
2.0	24	2.0	50

\*Viscosity expressed in centipoise, measured at 100rpm.



Fig. II Brookfield Viscosities

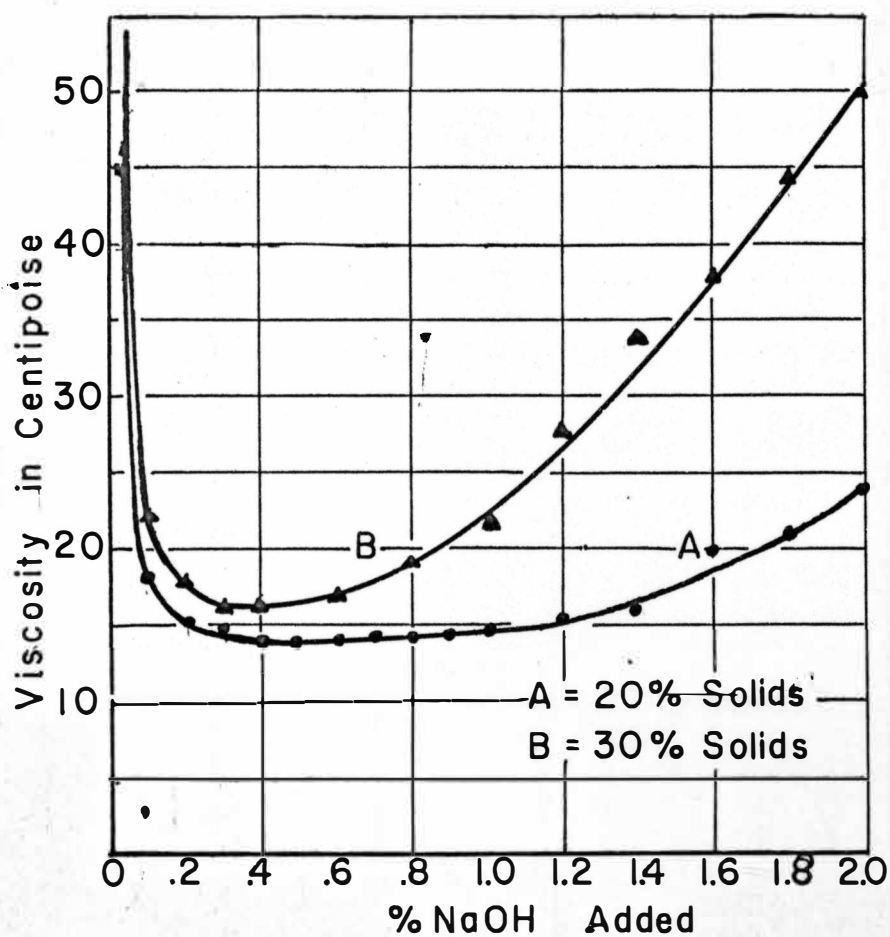


Fig. 12 Hercules Rheograms at 30% Solids

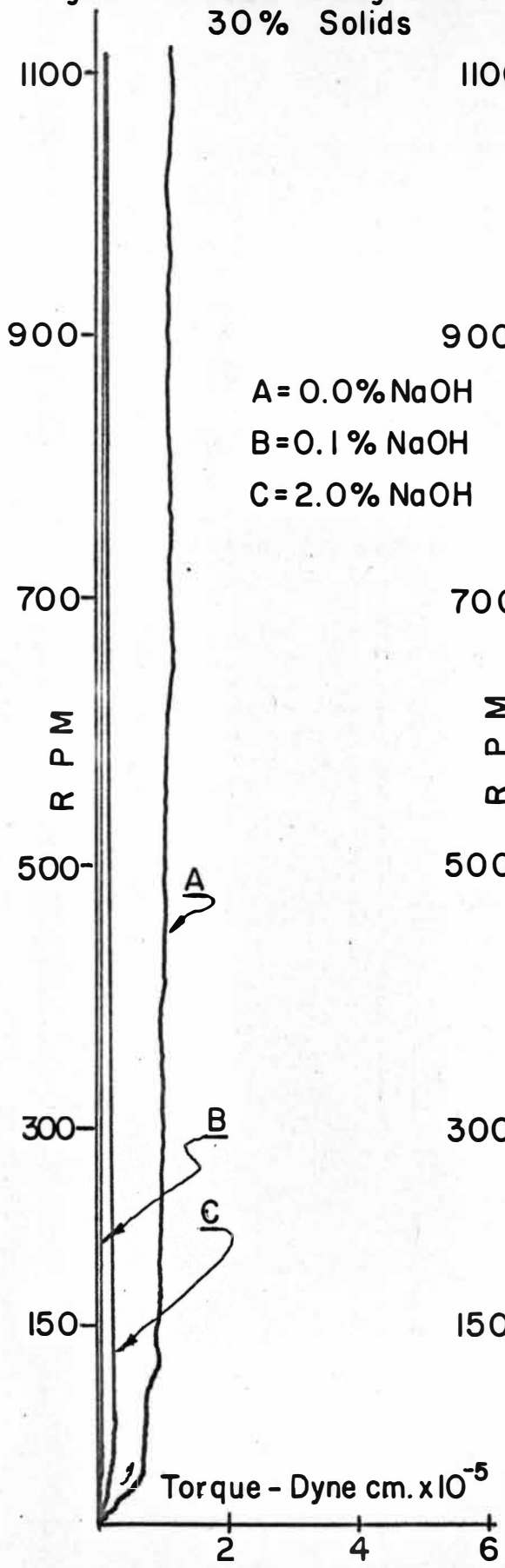
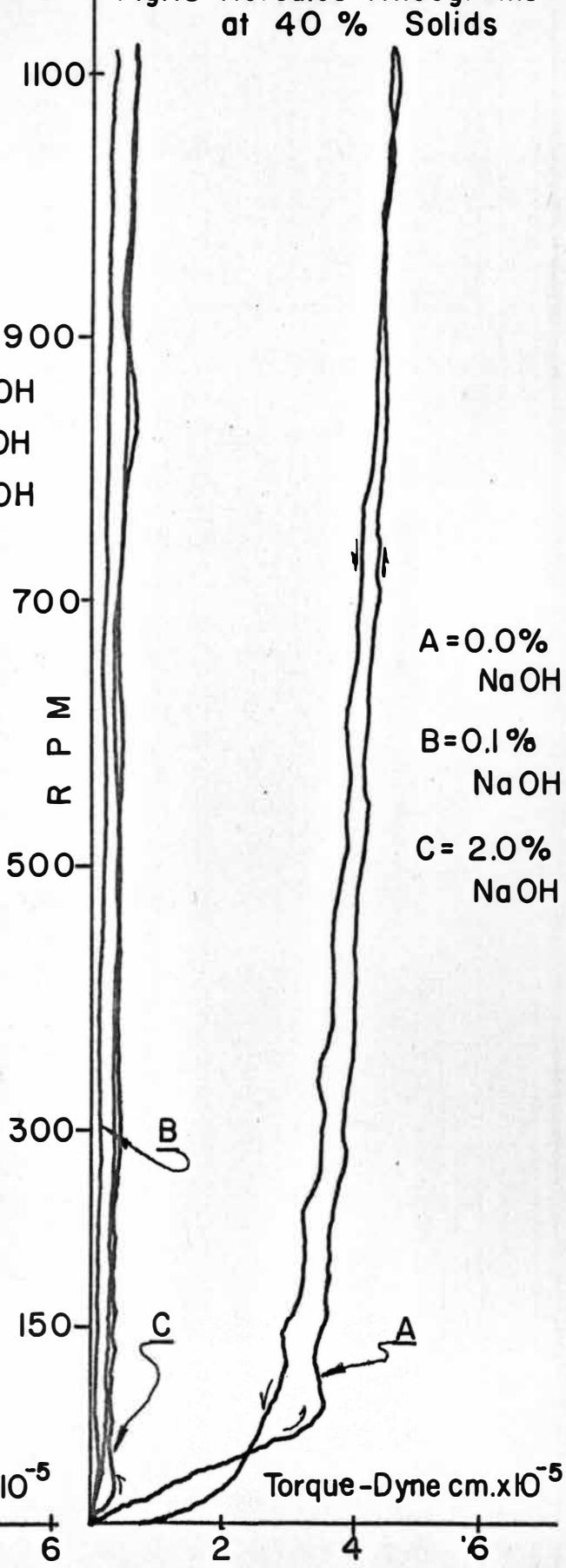


Fig. 13 Hercules Rheograms at 40% Solids



flocculation indicated here may be due to edge to face flocculation which, according to van Olphen<sup>11</sup>, will lead to a higher viscosity than face to face flocculation. The RSV data shown in Figures 3 through 10 do not indicate as great a difference between the flocculation at 0.00% NaOH and 2.00% NaOH as was indicated by the viscosity data or theoretical discussion.

It can therefore be concluded that although the RSV measurement is dependent on the degree of flocculation it is generally not as sensitive to small changes as is the viscosity measurement, furthermore RSV cannot satisfactorily differentiate between the different forms of flocculation believed to exist at high and low electrolyte concentrations.

#### The Applicability of the Verwey-Overbeek Theory

The results of the Verwey-Overbeek theory calculations are shown in Figures 14 through 21. The data is not included in tabular form due to the large amount of data generated as well as the difficulty in interpreting the data in tabular form. Each of the curves is drawn through points at  $0.1 \times 10^{-7}$  cm intervals between  $1.0 \times 10^{-7}$  cm and  $2.0 \times 10^{-7}$  cm, and at  $1.0 \times 10^{-7}$  cm intervals between  $2.0 \times 10^{-7}$  cm and  $15.0 \times 10^{-7}$  cm.

Fig. 14 Potential Energy Curves at 10% Solids

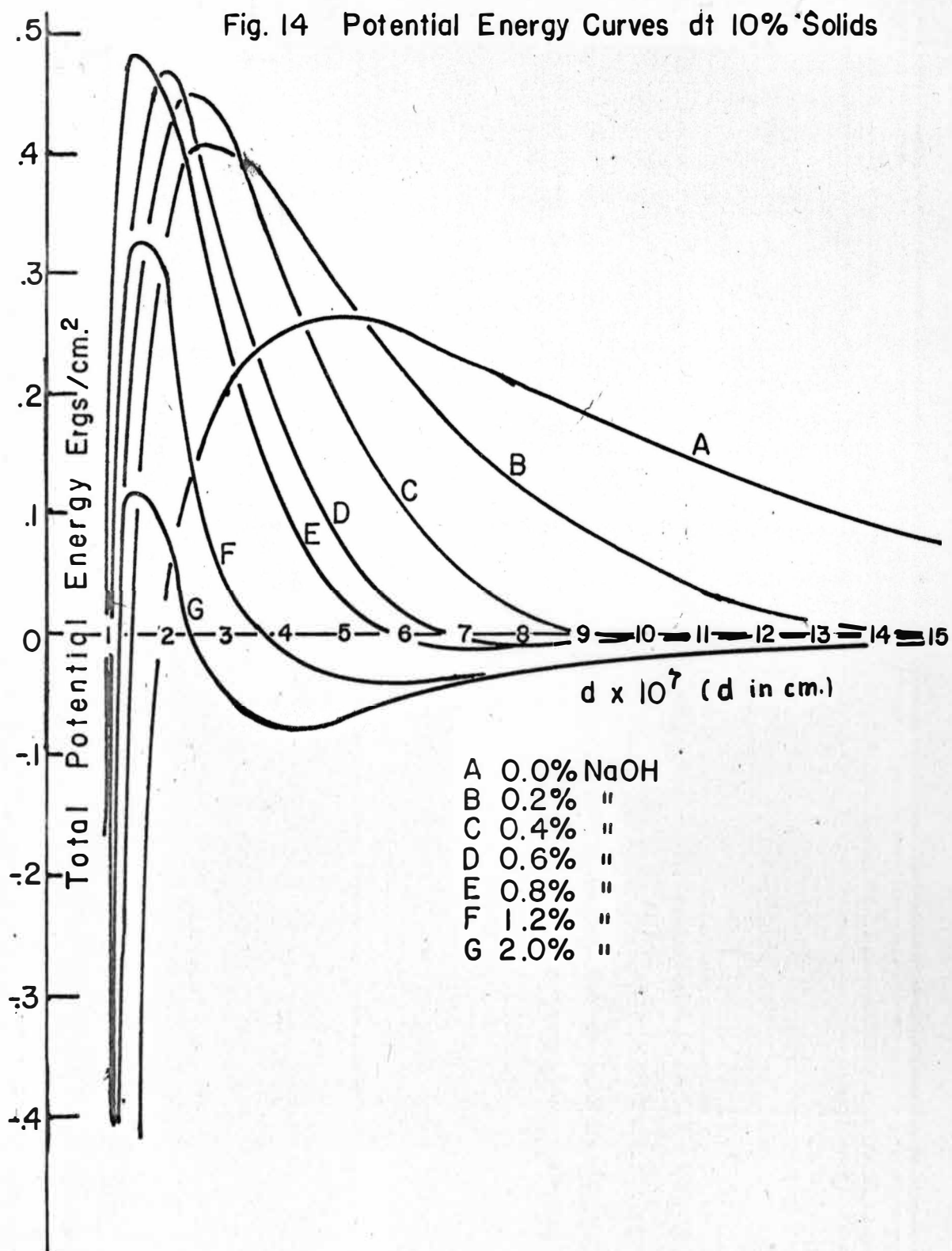


Fig. 15 Potential Energy Curves at 20% Solids

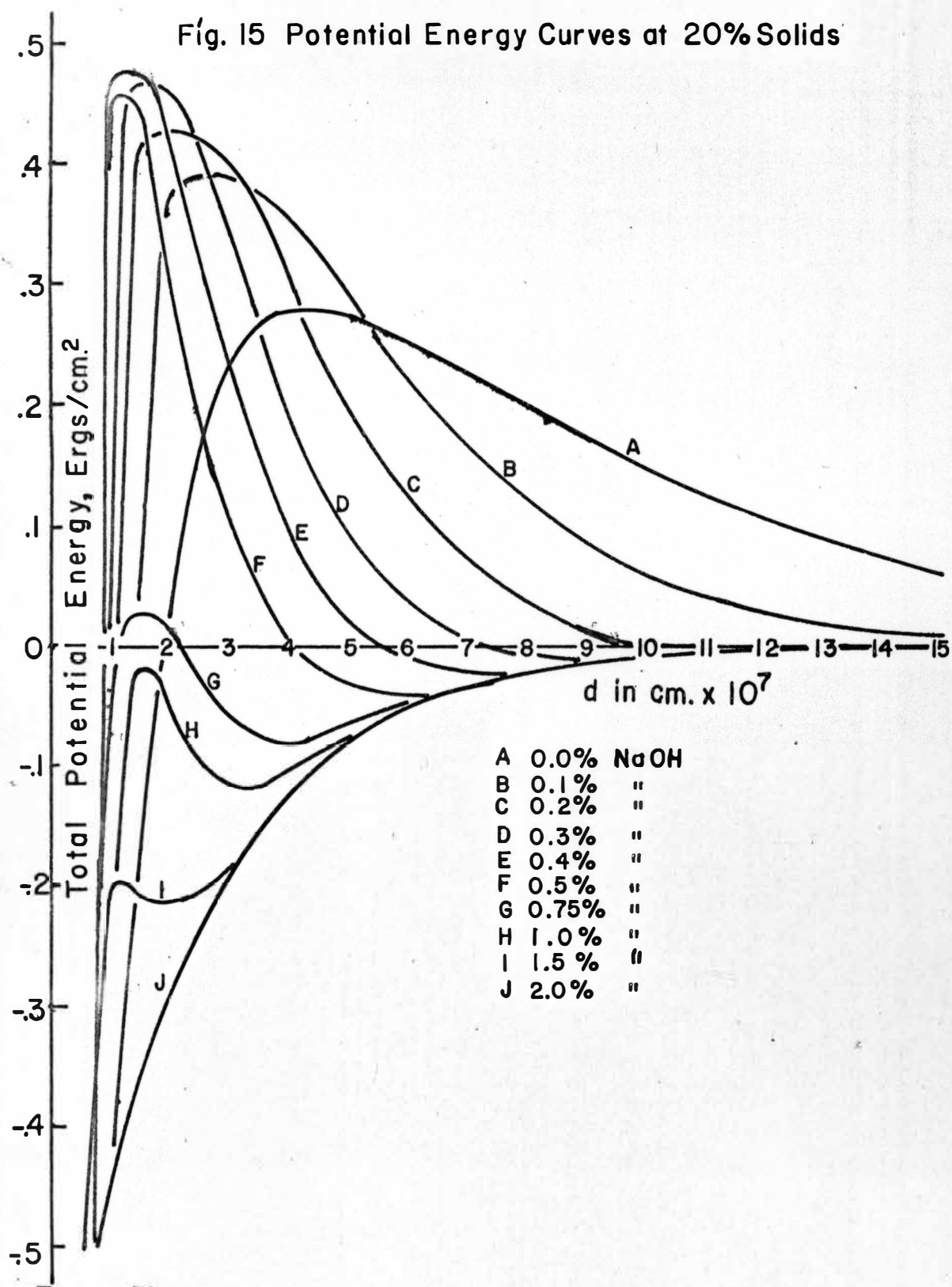


Fig. 16 Potential Energy Curves at 30% Solids

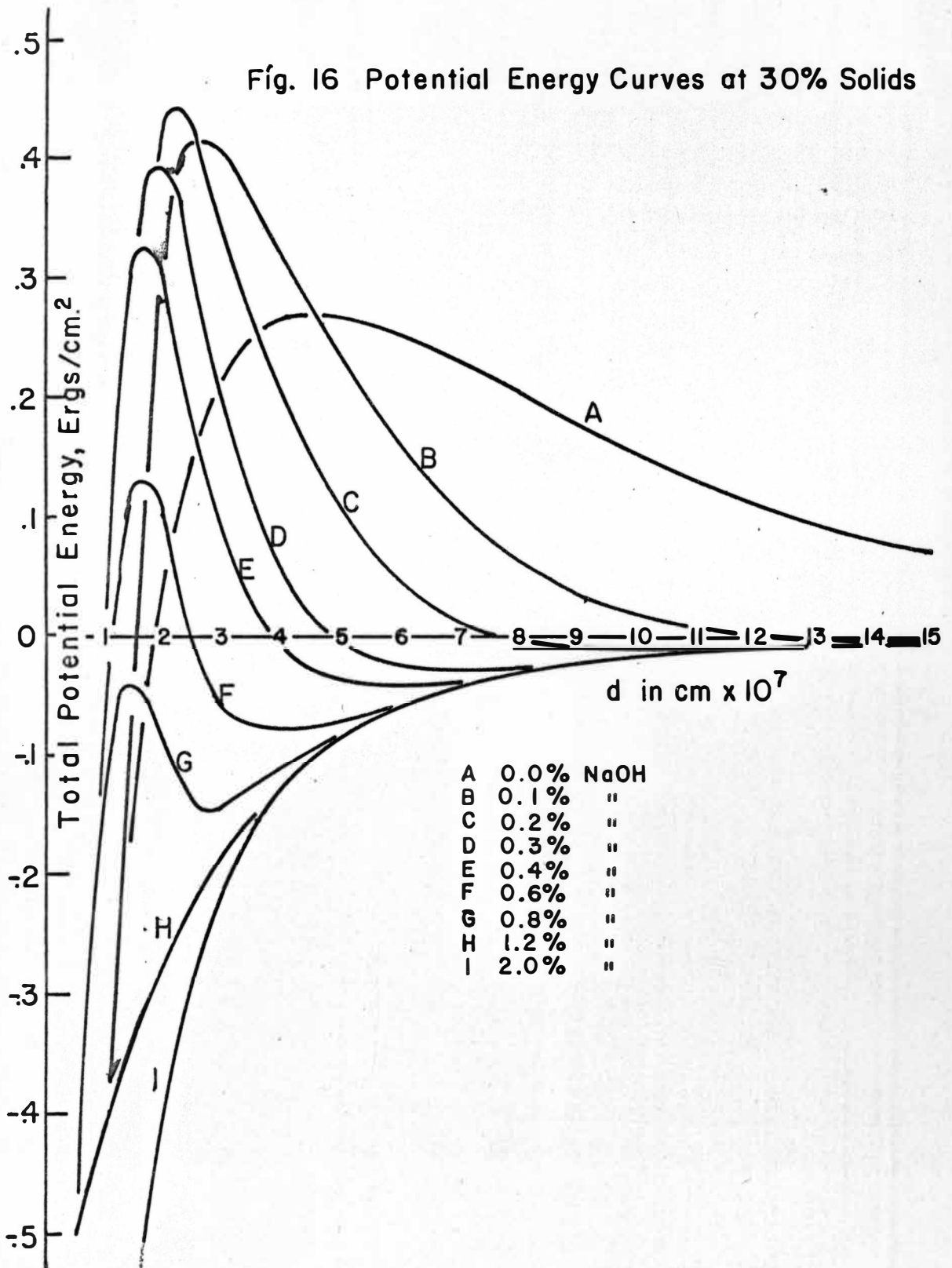


Fig.17 Potential Energy Curves at 40% Solids

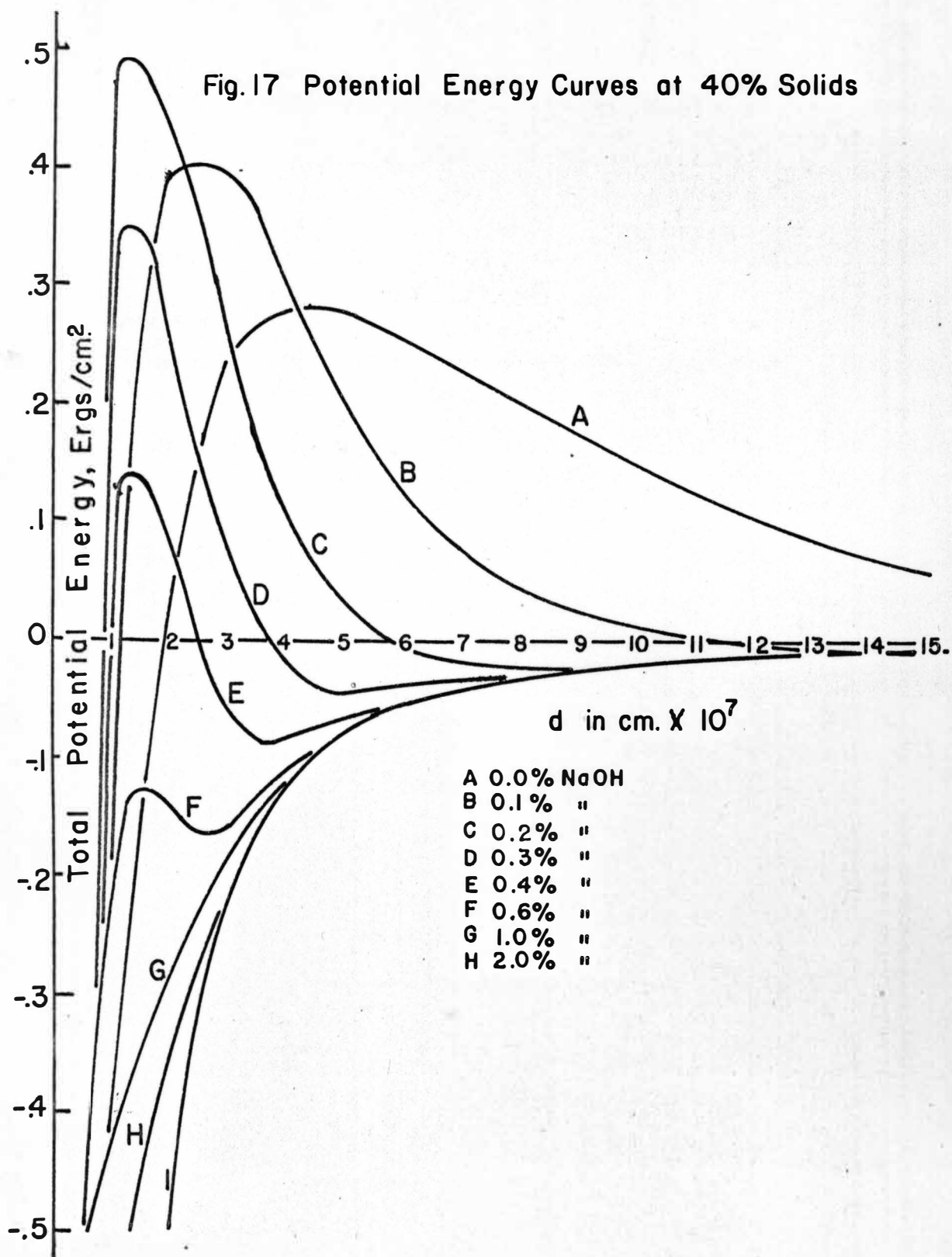


Fig. 18 Potential Energy Curves at 10% Solids

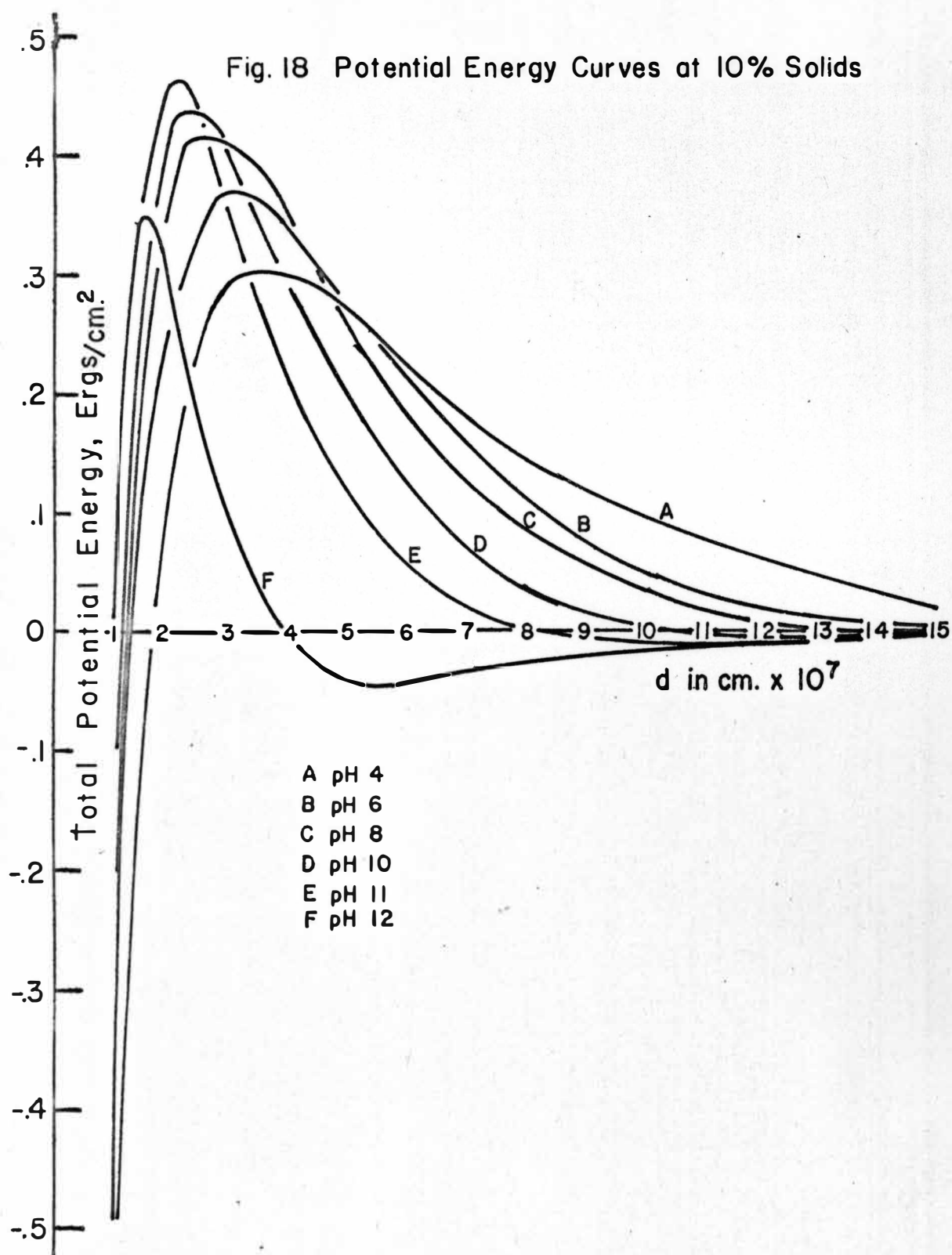




Fig. 19 Potential Energy Curves at 20% Solids

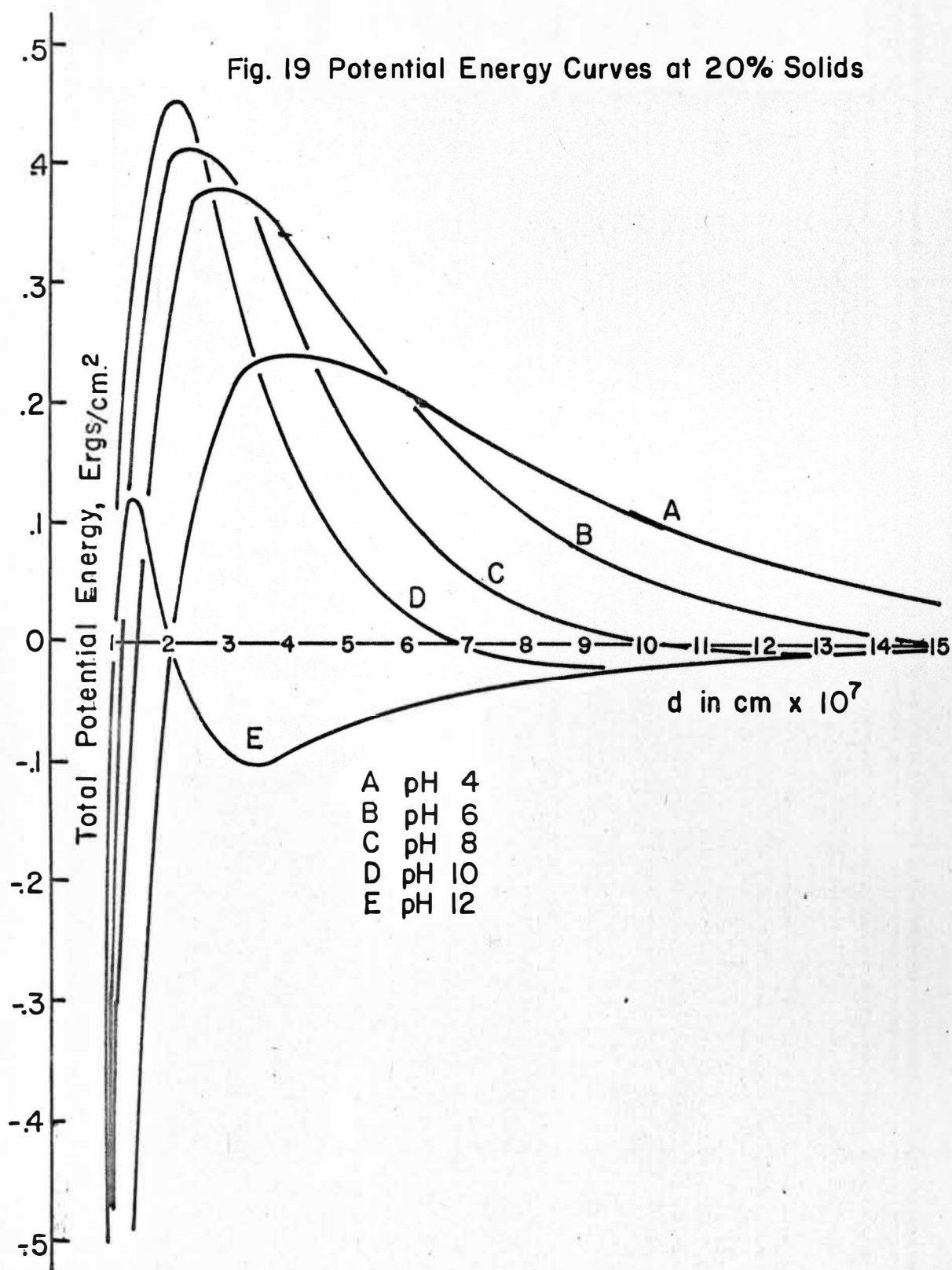


Fig. 20 Potential Energy Curves at 30% Solids

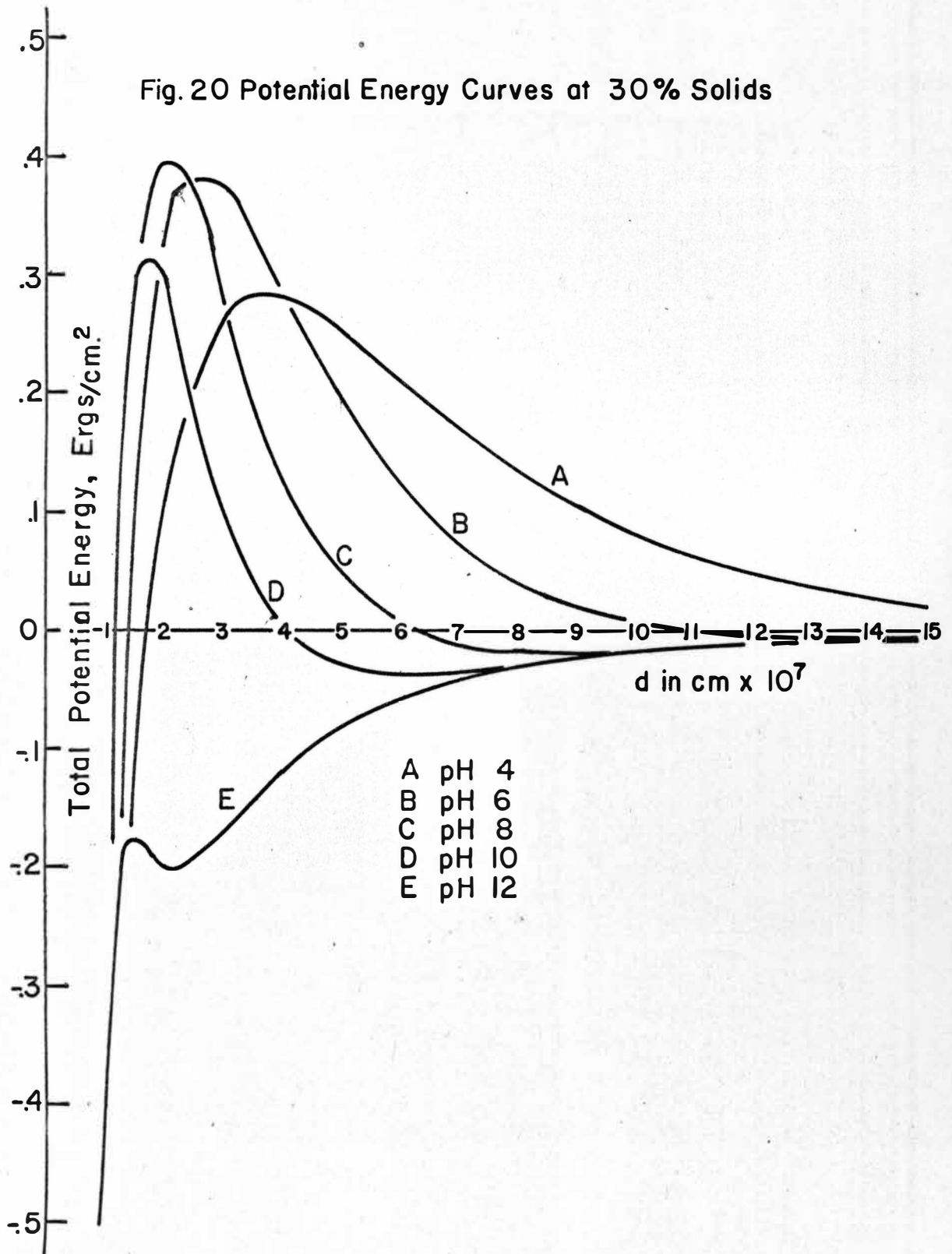
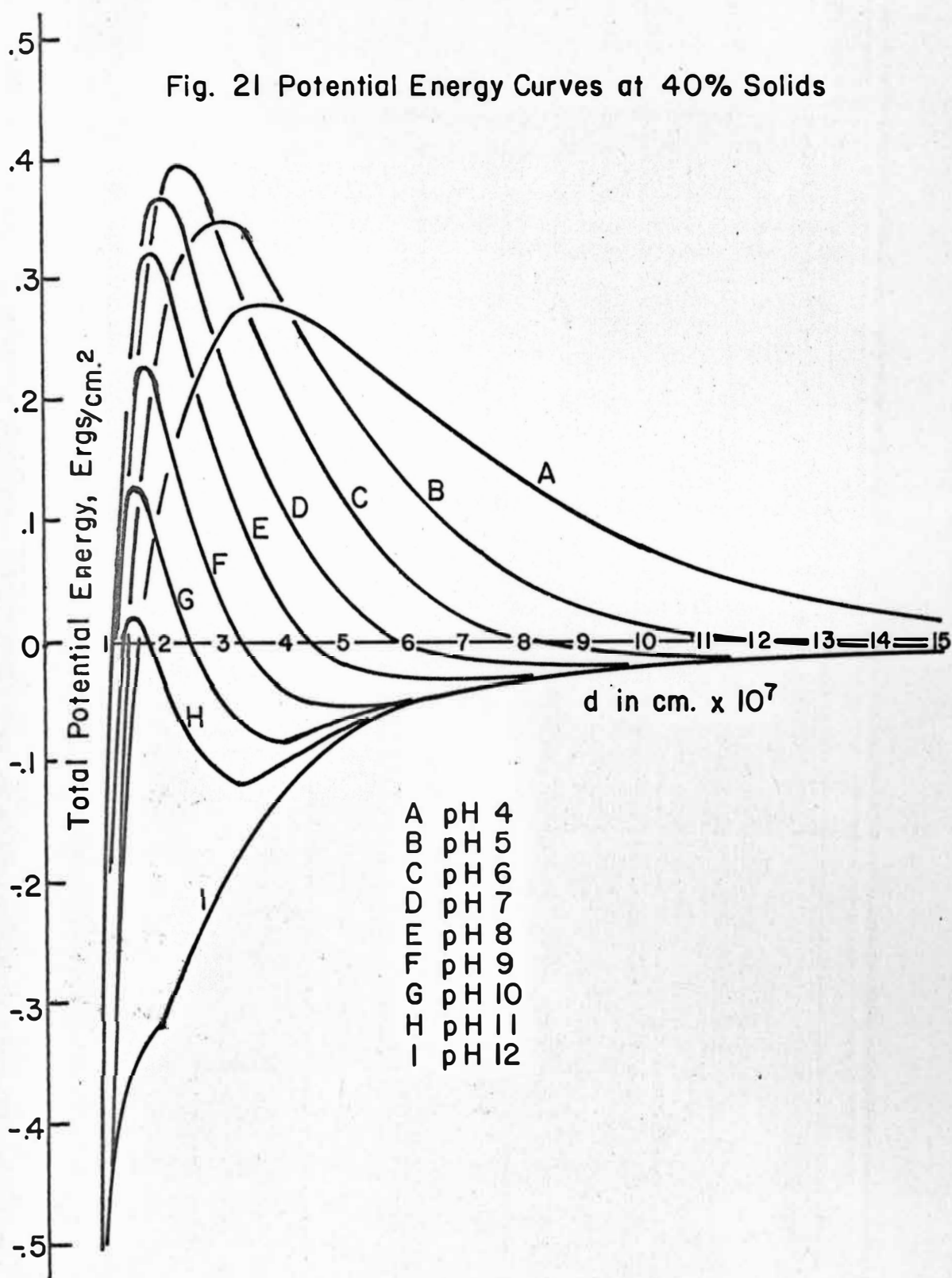


Fig. 21 Potential Energy Curves at 40% Solids



Cursory inspection of Figures 14 through 21 leads one to conclude that the Verwey-Overbeek theory predicts the effect of electrolyte concentration on stability observed in the RSV and viscosity data, in that as the electrolyte concentration is increased the stability is predicted to increase up to a point and then decrease. However, closer examination of the Figures shows that the agreement between the predicted and observed data is only qualitative, at best. Figures 14 through 17 predict that the 0.00% NaOH system should be more stable (less flocculated) than the 2.00% NaOH system, which prediction is in direct opposition to the results obtained with both the viscosity and RSV measurements.

The failure of the Verwey-Overbeek theory to predict a higher degree of flocculation at 0.00% NaOH than at 2.00% NaOH supports the belief that the plates are positively charged on the edges and negatively charged on the surfaces. The form of the repulsion potential function used incorporates calculated values for the electric surface potential ( $\gamma$ ). These values, through calculation of the surface charge density ( $\sigma$ ), are based on the assumption that the only charge on the particles is due to the adsorption of ions. The calculation of  $\sigma$  is based on the premise

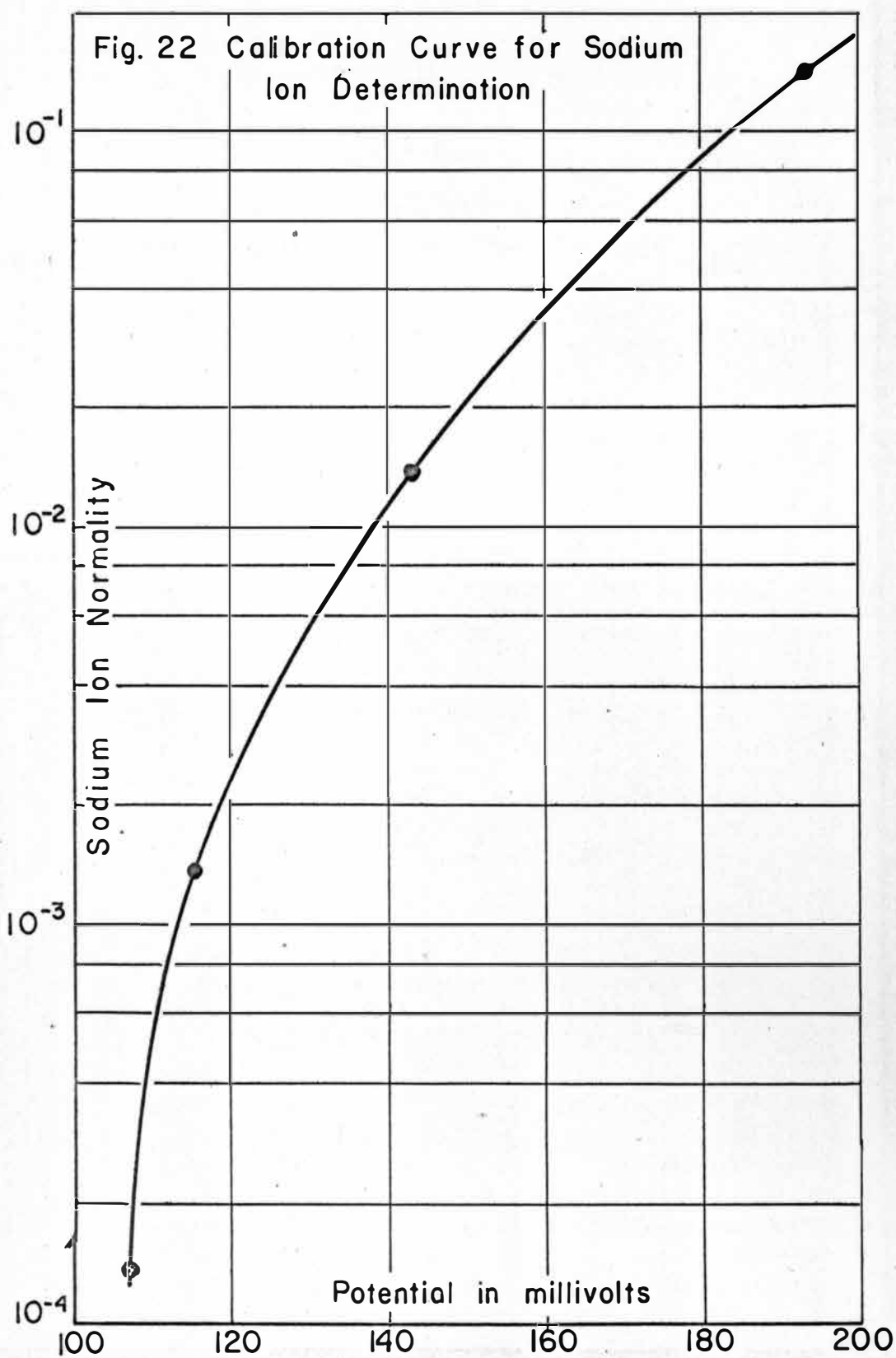
that all ions adsorbed by the particles go into formation of the electrical double layer, but if the edges of the plates are positively charged, the first ions adsorbed would go to neutralize the charge on the particles, and the theoretically calculated value for the meq. of anions adsorbed per gram of clay would be erroneously high. However, an error in the calculation of  $\sigma$  would have very little effect on the repulsion potential function as can be seen by examining how  $\sigma$  is applied in equations 13 through 17. Accordingly, although the reliability of the data might be improved by actual measurements of the surface charge density, it is unlikely that the specific problem at hand would be eliminated.

The biggest error in assuming that there is no charge on the edges of the plates would be in the expression used for the attraction potential. The expression used is based on the assumption that van der Waals-London forces apply, which expression was based on the particles being nonpolar. If indeed the particles are charged, the van der Waals-London forces definitely would not apply. However, if the first ions adsorbed neutralize the charge on the edges of the plates and the following ions build an electrical double layer which

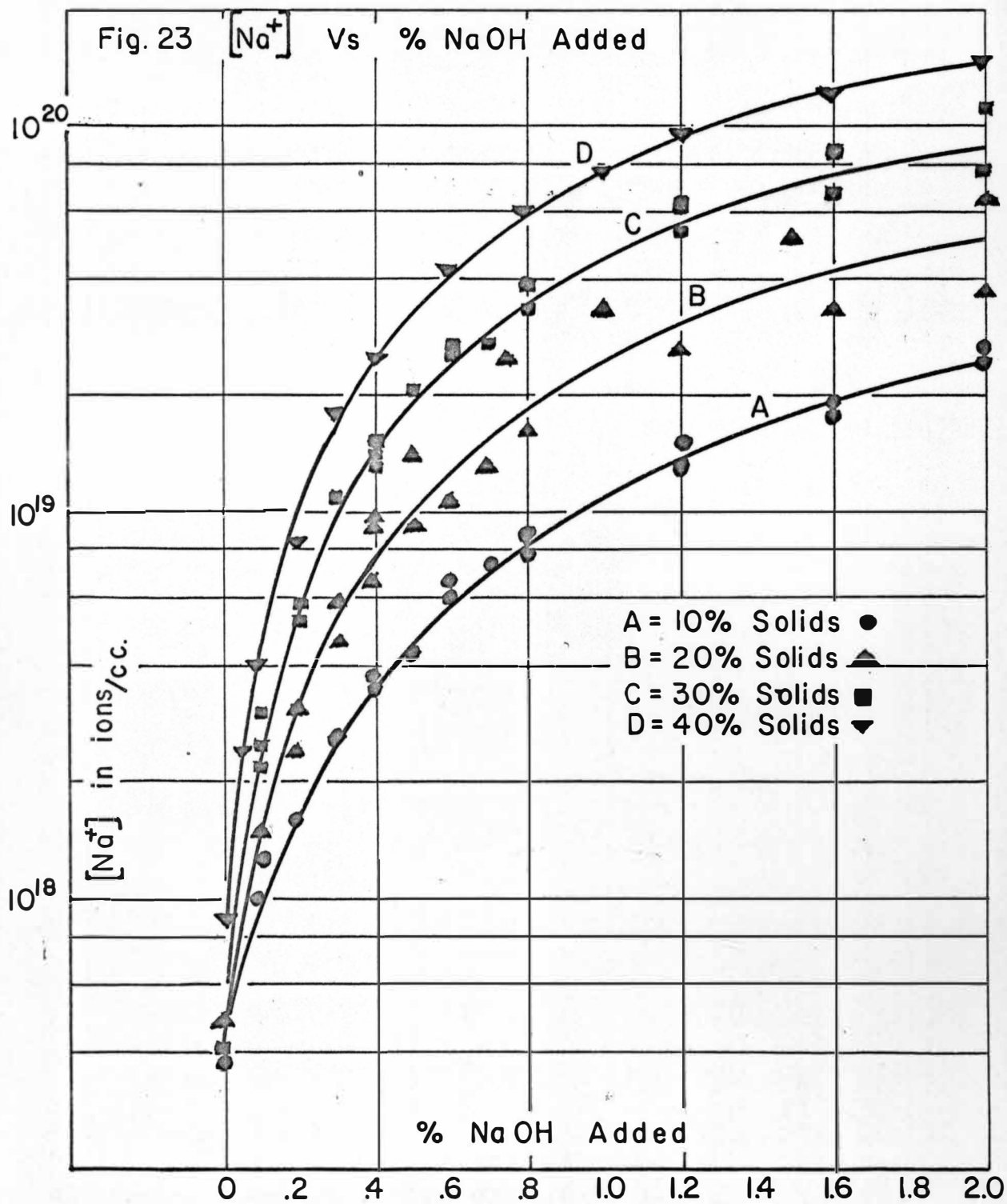
is more or less uniformly negative at the particle surface, or at least has the net effect of being uniformly negative at the particle surface, one might assume that the van der Waals-London forces would apply at higher electrolyte concentrations. Accordingly, such an assumption is fortified by the fact that the agreement between the predictions of the Verwey-Overbeek theory and the results of the stability tests contained in this paper are in quite good agreement at higher electrolyte concentrations. Therefore it is obvious that a different expression for the attractive potential, which took into account the charge on the plates at low electrolyte concentrations and placed decreasing importance on these charges as the electrolyte concentrations were increased, should give better agreement between the calculated and measured degree of flocculation. It can therefore be concluded that the Verwey-Overbeek theory has been shown to give qualitative agreement with the observed data, and could possibly be shown to give even better agreement if the proper functions for the attractive potential and better means of determining the electric surface potential were available.

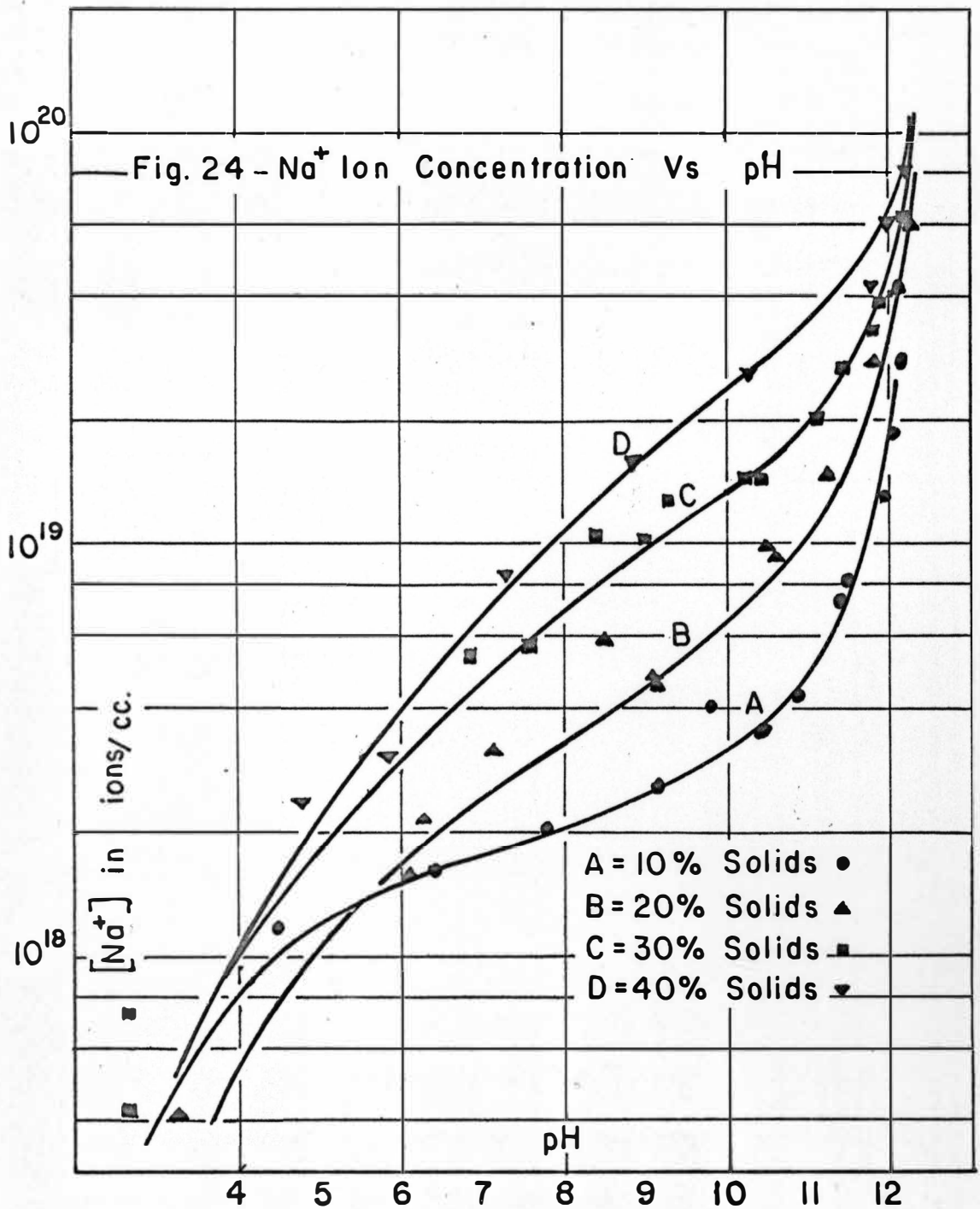
### Determination of the Sodium Ion Concentration

Figure 22 shows the analytical curve obtained for the potentiometric determination of the sodium ion concentration. The points plotted on Figure 22 are the values obtained on the standard solutions. The lack of linearity of the analytical curve might well be influenced by the buffering solution used. Use of the sodium ion electrode requires controlled pH conditions, therefore the standard solutions and the sample solutions were buffered by mixing with an equal volume of a solution which was 0.5M with respect to  $K_2HPO_4$  and 0.25M with respect to  $KH_2PO_4$ . The solutions therefore were about 0.37M with respect to potassium ion and between 0.0005M and 0.07M with respect to the sodium ion. Since the electrode used was about 1,000 times more sensitive to sodium than potassium ions, the potassium ion concentration is obviously high enough to influence the readings. Figures 23 and 24 show the sodium ion concentrations in ions per cubic centimeter at the various solids levels used, plotted in Figure 23 against the percent NaOH added and in Figure 24 against the pH of the dispersion.









### Determination of the Hydroxyl Ion Adsorption

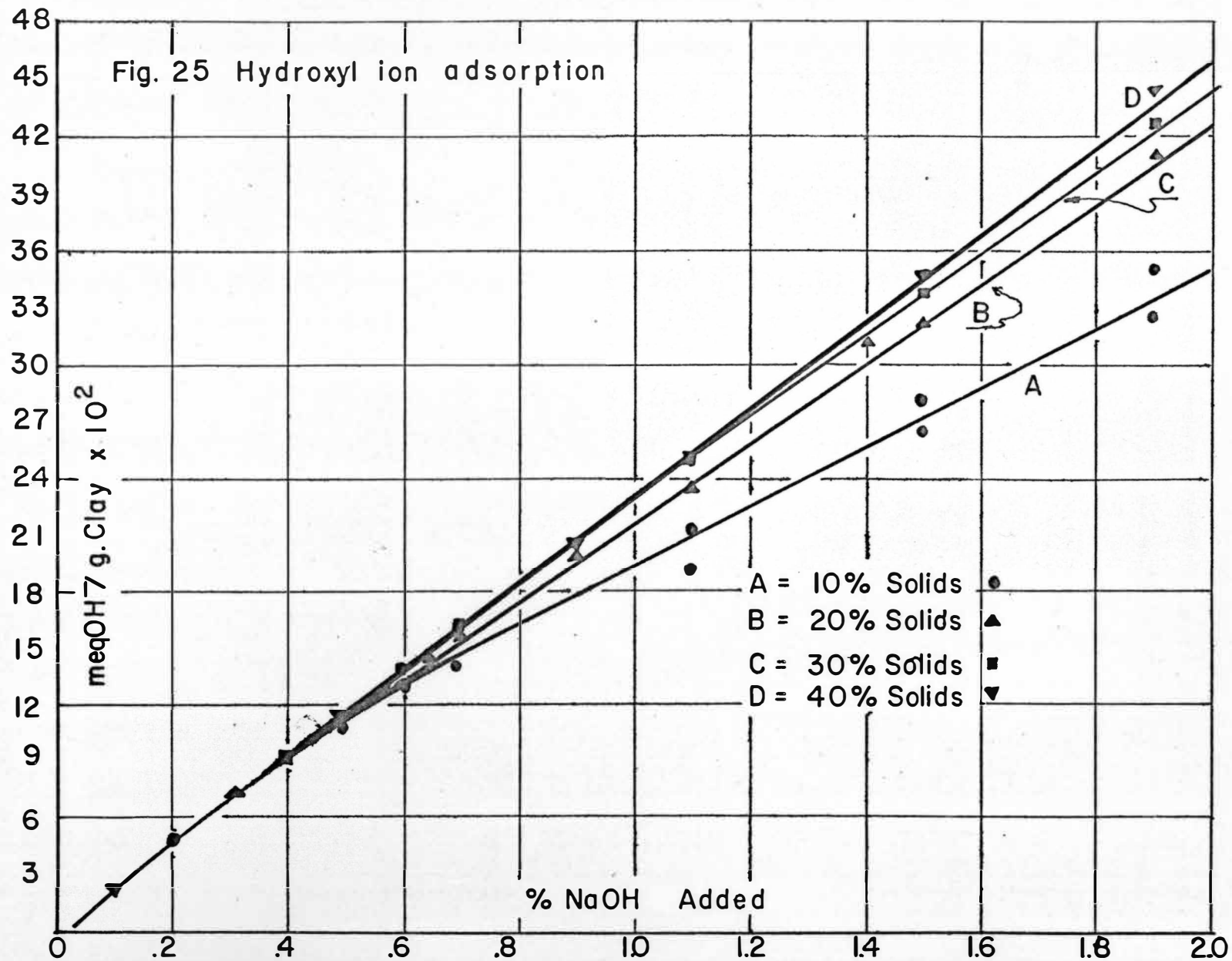
There were two methods used to calculate the hydroxyl ion adsorption. The first method was the direct calculation of the hydroxyl ion concentration in the intermicellar solution from pH measurements on the supernate from the centrifuging process. Having thus determined the intermicellar solution concentration, the amount of adsorption could be calculated through a material balance, assuming that any ions not in solution were adsorbed on the clay. The data obtained by this method are shown in Figure 25.

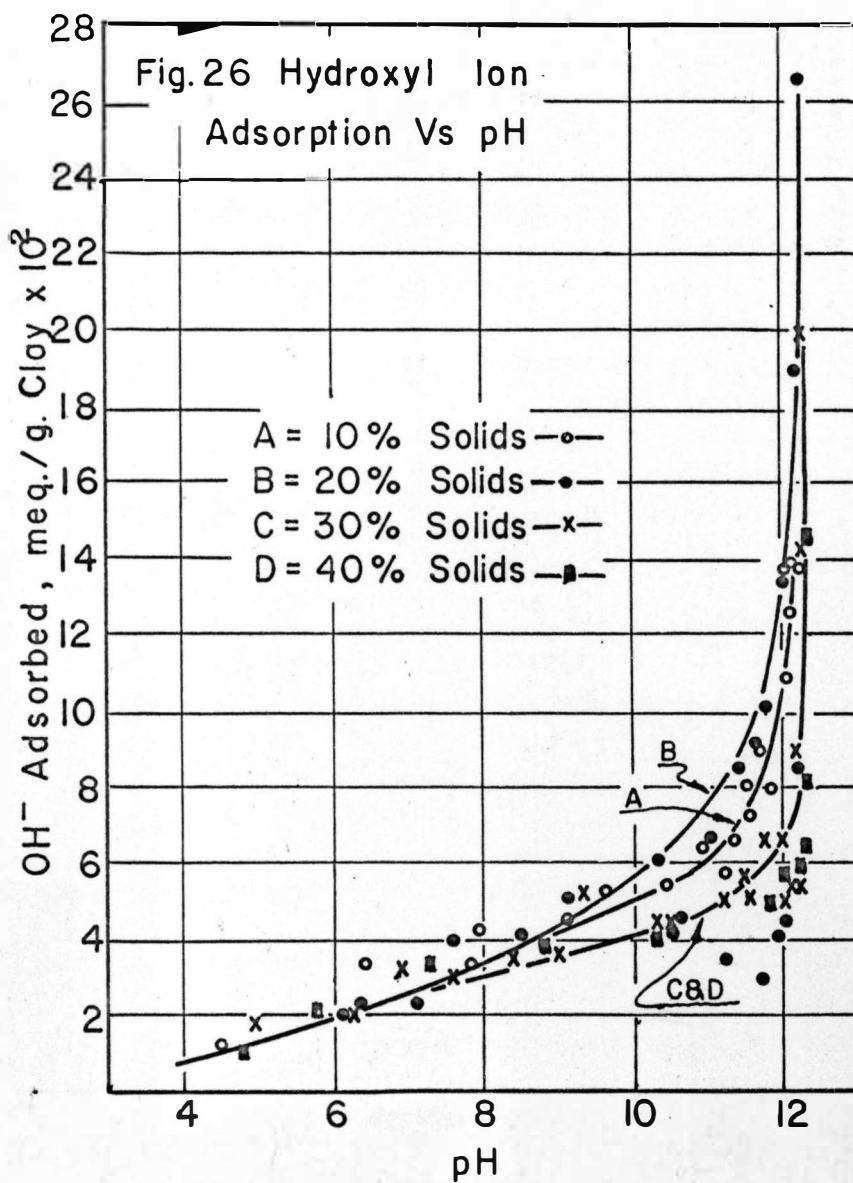
The second method of calculation was to assume that for every sodium ion in solution there is an hydroxyl ion in solution. The intermicellar solution concentration of hydroxyl ions is therefore equal to the sodium ion concentration, and the hydroxyl ion adsorption can again be calculated by a material balance. The data from this method are in Figure 26.

Comparison of the two techniques shows higher values for the data calculated from pH data. If adsorption values in Figure 25 had been plotted against pH, the curves would have been very similar to the curves in Figure 26. Therefore, the obviously poor correlation of data shown by the scatter of points in Figure 26

would also have been displayed for the pH calculated data.

When the data obtained from the two processes are used in the Verwey-Overbeek calculations the results are surprisingly similar. Figures 14 through 17 were based on the pH calculated values shown in Table I, and Figures 18 through 21 were based on values for hydroxyl ion adsorption interpolated from Figure 26 and sodium ion concentration values interpolated from Figure 24. It can be seen that there is very little difference between the predictions based on these two methods of hydroxyl ion adsorption calculation.





Determination of Pyrophosphate  
Not Removed by Deionization

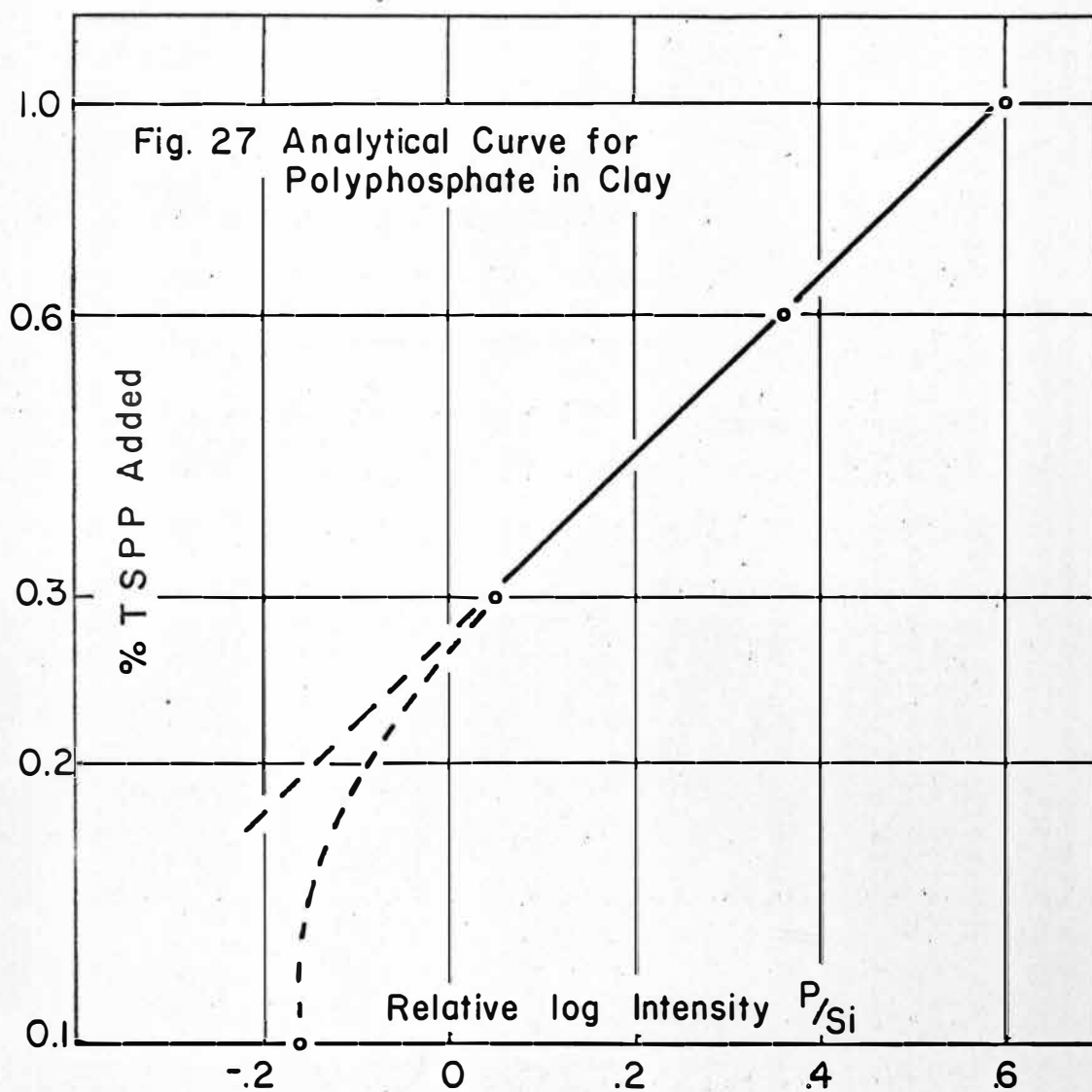
The amount of tetrasodium pyrophosphate (TSPP) remaining after deionization can not be determined by comparison to standard levels of addition since clay samples with no TSPP present were not available. Consequently the analyses were performed by a standard addition technique described by Nachtrieb.<sup>10</sup> The technique used obtained a non-linear plot of log % TSPP added versus the log of the ratio of the intensities of the phosphorous 2535.7 Å line to the silicon 2528.5 Å line. If no phosphorous were present in the original sample the plot would be linear, and if phosphorous were present, the plot would be concave to the lower right.

If a concave plot is obtained the % TSPP values are increased by equal increments along the entire plot until a linear plot is obtained. The amount of TSPP initially present is then equal to the amount the % TSPP values had to be increased in order to yield the linear plot.

The analytical curve shown in Figure 27, does not allow a definite conclusion since the upper portion is linear indicating that the sample was free of TSPP, however, the lowest point does not lie on the straight

line, indicating about 0.10% TSPP still present on the clay particles. Assuming 0.10% TSPP on the clay, the meq/g of adsorbed anion should be calculated and added to the hydroxyl ion adsorption. This calculation yields 0.0017 meq/g of phosphate which value has been added to the values listed in Table I.





## CONCLUSIONS

It has been shown that although the measurement of the relative sediment volume of a kaolin-water dispersion will give an indication of the degree of flocculation of the dispersed system it should not be accepted as a valid test for the stability of the dispersion under all conditions. This conclusion is based on the observations that the relative sediment volume measurement is not as sensitive to changes in the degree of flocculation as are viscosity or rheological measurements, and that the relative sediment volume measurement is inadequate in determining the different forms of flocculation believed to be occurring at high and low electrolyte concentrations. Further discussion is presented which discredits acceptance of the technique as anything more than a comparative test and explains the inherent problems in the various analytical techniques employed.

The predictions of the Verwey-Overbeek theory have been shown to be in qualitative agreement with the

observed results. Discussion of the areas where the theory fails to apply, point out that the lack of agreement is most likely due to the unavailability of an expression for the attractive potential which takes into consideration the attractive forces other than London forces, and the unavailability of adequate means of determining the electric surface potential of the plates. It can therefore be concluded that the Verwey-Overbeek theory probably does apply to kaolin-water systems, as evidenced by the good qualitative agreement shown in this paper.

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## APPENDIX I

Solutions to the Verwey-Overbeek theory equations were obtained through the Fortran program displayed on page 66. The second through ninth cards feed the necessary constants into the computer and are explained in the parentheses. The statements which are numbered on the left as 6 through 5 inclusive, instruct the computer to read the data cards, test the first bit of data to see if the card being read is the last data card (in which case calculation would be terminated), if calculation is to be continued, the computer is instructed to punch a card which will identify the ensuing output data. The input data cards contain 1. the pH of the dispersion (Y), 2. the percent solids of the dispersion (Q), 3. the intermicellar concentration of counter ions (C) and 4. the meq/g of anions adsorbed on the surface of the clay (Z). The first two bits of data are not used in the calculations, but are used in the preparation of the data identification card.

The statements between statements 5 and 9 find

solutions to the parameters which are not influenced by the distance of separation of the particles. Statements 9 through 7 inclusive, generate values for the parameter d, (called H in the program) which is one half the distance of separation between the plates. The remainder of the program concerns the calculation of the repulsive potential energy (VR), the attractive potential energy (VA) and the total potential energy (TV). The last three values are then punched in the proper columns along with the value of d (H) upon which they were calculated. The solution incorporated in this program is the same as the method of solution described on pages 11 through 16 in the text of this paper.

The constant (A) was evaluated by Holtzman<sup>4</sup> to be  $4 \times 10^{-12}$ , however, this constant was re-evaluated to  $3 \times 10^{-12}$  to give a better fit of the data in this paper.

The Fortran program used is displayed on the following page, and followed on the next page by a sample of the solution data. The sample solution data shown was used to plot the pH 8 curve in Fig. 21. All of the curves in Figures 14 through 21 were based on similar sets of data.

## FORTRAN PROGRAM FOR THE SOLUTION OF THE VERWEY-OVERBEEK THEORY

```

ZZFORX54      JAMES E. KLINE SOLUTION TO V+O THEORY PH FORM FINAL
      PI=3.14      ( $\pi$ )
      BK=1.38E-16  (the Boltzmann constant)
      E=4.80E-10   ( $\epsilon$ )
      D=78.9       (the dielectric constant of water)
      AN=6.02E+20  (Avogadro's no.)
      AS=1.15E+5   ( $a'$ )
      A=3.0E-12    ( $A$ )
      T=293.0      ( $^{\circ}K$ )
      V=1.0        (the valence of the counter ion)
6      READ 1,Y,Q,C,Z
1      FORMAT(F5.2,2X,F5.2,2X,E9.3,2X,F10.6)
      IF(Y-15.0)2,10,10
2      PUNCH 3,Y,Q
3      FORMAT(15H WITH A PH OF,F5.1,2HAT,F7.2,15H PERCENT SOLIDS)
      PUNCH 4,C,Z
4      FORMAT(3H C=,E9.3,5X,2HZ=,F10.6)
      PUNCH 5
5      FORMAT(5X,1HH,8X,2HVA,8X,2HVR,9X,2HTV)
      SIG=AN*E*Z/AS
      P=SIG*SQRTF(PI/(2.*D*BK*T*C))
      B=P+SQRTF(P**2+1.)
      G=(B-1.)/(B+1.)
      X=SQRTF((8.*PI*C*E**2*V**2)/(D*BK*T))
      H=16.0E-7
      J=1
9      H=H-(1.0E-7)
      IF(H-2.0E-7)16,16,7
16     H=2.1E-7
      J=2
11     H=H-(0.1E-7)
      IF(H-0.9E-7)6,6,7
7      CONTINUE
      VA=(-A)/(48.*PI*H**2)
      U=X*H
      TANHU=(EXP(U)-EXP(-U))/(EXP(U)+EXP(-U))
      VR=((32.*C*BK*T*G**2)/X)*(1.-TANHU)
      TV=VA+VR
      PUNCH 8,H,VA,VR,TV
8      FORMAT(E8.1,F9.4,2X,F9.4,2X,F9.4)
      GO TO (9,11),J
10     CALL EXIT
      END

```

WITH A PH OF 8.0AT 40.00 PERCENT SOLIDS  
 C= .110E+20 Z= .030000

H	VA	VR	TV
1.5E-06	-.0088	0.0000	-.0088
1.4E-06	-.0101	0.0000	-.0101
1.3E-06	-.0117	0.0000	-.0117
1.2E-06	-.0138	.0001	-.0136
1.1E-06	-.0164	.0003	-.0161
1.0E-06	-.0199	.0007	-.0191
9.0E-07	-.0245	.0018	-.0227
8.0E-07	-.0311	.0044	-.0266
7.0E-07	-.0406	.0107	-.0298
6.0E-07	-.0552	.0262	-.0290
5.0E-07	-.0796	.0637	-.0158
4.0E-07	-.1244	.1533	.0289
3.0E-07	-.2211	.3605	.1394
2.0E-07	-.4976	.8064	.3088
1.9E-07	-.5513	.8701	.3187
1.8E-07	-.6143	.9378	.3235
1.7E-07	-.6887	1.0097	.3210
1.6E-07	-.7775	1.0859	.3083
1.5E-07	-.8846	1.1663	.2817
1.4E-07	-1.0155	1.2510	.2355
1.3E-07	-1.1777	1.3401	.1623
1.2E-07	-1.3822	1.4334	.0511
1.1E-07	-1.6449	1.5309	-.1140
1.0E-07	-1.9904	1.6324	-.3579