

# FORCES BETWEEN SUSPENDED BENTONITE PARTICLES<sup>1</sup>

*By*

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## ABSTRACT

Purified sodium bentonite suspensions in water display rigidity at concentrations as low as about 2 percent. On addition of NaCl the yield stress decreases, but beyond about 5 meq/liter of NaCl it increases. The same is true for the relative viscosities and the sediment volumes of more dilute suspensions. This is interpreted as a flocculation-deflocculation-flocculation sequence. The paradoxical phenomenon of flocculation of the clean suspensions is explained by the concept of positive edge charge of the clay plates, allowing positive edge to negative flat-surface flocculation.

Both the purified and the salt-flocculated gels show Bingham flow behavior. When Good-ave's analysis of Bingham flow is applied, the linking force between the clay plates in the pure gels is computed at about  $10^{-4}$  dyne.

The salt-flocculated gels show thixotropic hysteresis, whereas the pure gels set immediately after stirring. This means that there is no energy barrier for gelation in the pure gels, which is in line with the proposed mechanism of association due to Coulomb attraction. In the salt-flocculated gels there must be an energy barrier causing thixotropic hysteresis. This might be expected from the summation of residual double-layer repulsion and van der Waals attraction. Considering thixotropic stiffening as slow coagulation, the height of the energy barrier could be calculated from the thixotropic increase of the modulus of elasticity with time after previous shear breakdown of the structure. The reasonable value of  $7 kT$  was found for the height of the energy barrier of a gel containing 30 meq/liter of NaCl.

## INTRODUCTION

Suspended clay particles are commonly of submicroscopic size. Various kinds of forces act between them. These may be either repulsive or attractive and, depending on their balance, the particles may either attract each other and agglomerate or repel each other and remain separated.

Quite generally a concentrated "flocculated" suspension, in which attractive forces predominate, displays a yield stress which is caused by the formation of a rigid scaffolding structure. On filtration or sedimentation of dilute suspensions these structures are preserved, amounting to thick permeable filter cakes and large sediment volumes. In a "peptized" suspension, on the other hand, where repulsive forces predominate, no structure formation and yield stress development takes place and the suspension flows easily at moderate concentrations. On filtration or sedimentation of dilute suspensions the particles can slide along each other and attain a rather compact filter cake or sediment.

Although these relations are generally true for all suspensions of solids, the effects are quite pronounced in the case of clays because the clay particles are commonly large thin flakes. In principle, in suspensions of such platelike particles, three different types of association can occur. There can be association

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between the flat surfaces, or between the edges, or between the edges of one particle and the flat surface of another particle. In particular, the latter two will form voluminous scaffolding structures which are primarily responsible for the rheological and sedimentation behavior mentioned above.

The forces governing the flat surface association have been discussed extensively in a previous paper (van Olphen, 1954). In the present communication, the emphasis will be on the forces governing edge-to-edge and edge-to-flat surface association.

## PREPARATION OF SYSTEMS

Two pure sodium Wyoming bentonite suspensions were prepared by resin column conversion of raw Wyoming bentonite and subsequent washing in the ultracentrifuge. One suspension (*T*) contained all matter smaller than an equivalent spherical radius of 2 microns; the other suspension (*F*) was obtained by removal of the coarser part of suspension *T* in the ultracentrifuge.

Portions of different clay concentrations were prepared from both suspensions by sedimentation in the ultracentrifuge. Portions of constant clay concentration and different NaCl concentrations were also made up.

## RHEOLOGICAL OBSERVATIONS

### *Concentrated Suspensions*

*Modified Stormer viscometer.*—The rheological behavior of the more-concentrated suspensions showing plastic behavior was determined by the modified Stormer viscometer (van Olphen, 1950, p. 223). The suspensions followed very closely Bingham plastic flow with deviations occurring below a shear rate of about  $100 \text{ sec}^{-1}$ . In a plot of the rate of rotation versus driving torque, straight lines are obtained at sufficiently high rates of shear (Fig. 1). From the slope of the line the differential viscosity can be obtained. From the intersection of the extrapolated straight line with the torque ordinate the Bingham yield stress can be computed. With the apparatus constants, the differential viscosity can be expressed in centipoises and the Bingham yield stress in dynes/cm<sup>2</sup>.

In Figure 2 the Bingham yield stress is plotted versus the clay concentration for the *T* and *F* suspension as well as for the *F* suspension containing 60 meq/liter NaCl. The curves show that the yield stress appears to be rather sensitive to clay concentration changes in all three cases.

At the right in Figure 2 the variation of the yield stress with the amount of salt added at 3.22 percent by weight of *F* suspension is presented. A sharp drop of the yield stress on addition of a little salt is followed by a rise when more salt is added.<sup>1</sup>

In Figure 3 analogous plots are presented for the differential viscosity. It appears that the viscosities for the three systems tested are roughly the same within about plus or minus 10 percent, and changes in clay concentration or salt concentration have much less effect on viscosity than on yield stress.

<sup>1</sup> The yield stress of the pure suspensions decreases when the gel is left in contact with metals. Therefore the Stormer viscometer was plastic-coated for these experiments.

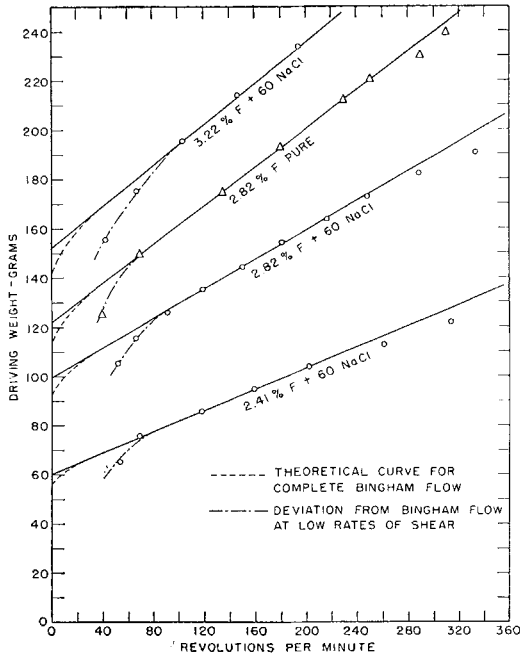


FIGURE 1.—Bingham flow curves obtained with the modified Stormer viscometer.

Figure 4 shows that the clay concentration dependence of the Bingham yield stress  $\tau_B$  can be fitted in the form

$$\tau_B = k(c - c_m)^2 \quad (1)$$

by choosing a proper value of  $c_m$ , where  $c$  is the weight concentration of the clay and  $k$  and  $c_m$  are constants. The values of  $k$  and  $c_m$  for the three suspensions are tabulated in the figure. The significance of this plot will be discussed later.

*Shear propagation.*—The coefficient of elasticity of the bentonite gels was determined from the velocity of propagation of a shear wave through the gel. The amount of shear was so small that the elastic limit of the gel was not exceeded: the velocity was independent of the amount of shear (amplitude) in the range studied. If the velocity of propagation  $V$  is known, the modulus of elasticity  $\mu$  is obtained from

$$\mu = \rho V^2 \quad (2)$$

where  $\rho$  is the density of the suspension.

The apparatus developed by W. L. Roever of this laboratory consists of a cylinder which contains the gel, with a transducer at each end. The transducers are modified phonograph pickups, so arranged that they generate or respond to shear motion.

A sharp, low-amplitude shear wave is generated at one end of the sample-container and the disturbance travels to the receiver pickup and is displayed on a cathode ray tube. The display, which includes timing markers, is photographed with a Land camera.

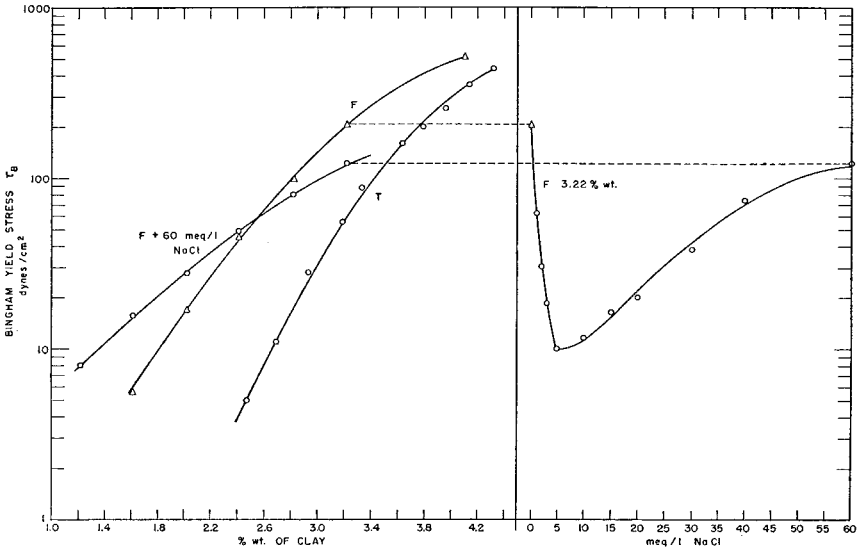


FIGURE 2.— Bingham yield stress as a function of clay concentration and amount of NaCl added.

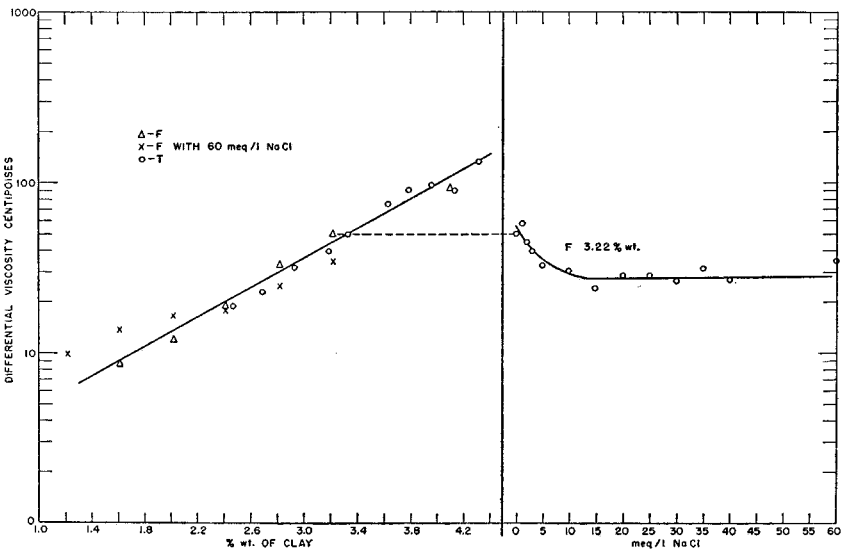


FIGURE 3.— Differential viscosity as a function of clay concentration and amount of NaCl added.

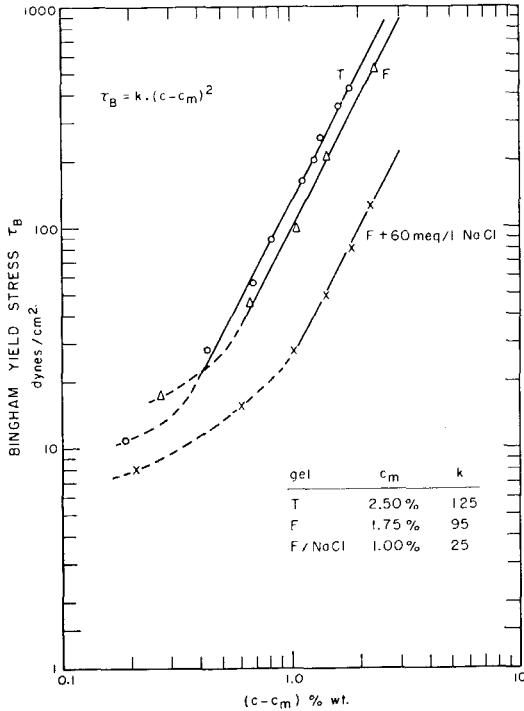


FIGURE 4. — Bingham yield stress as a function of  $(c - c_m)$ .

For the  $F$  suspension without salt, the arrival times of the pulses at different travel distances were determined at several clay concentrations.

The results are given in Figure 5, where for each concentration the arrival time is plotted versus the traveling distance. From the slopes of the lines the velocity of propagation and, from this, the modulus of elasticity are computed. The data are reported in the figures.

The modulus of elasticity rises rapidly with increasing clay concentration. With the same value  $c_m$  as found in the Bingham yield stress plot, the following relation between modulus of elasticity,  $\mu$ , and clay concentration  $c$  is found;

$$\mu = k'(c - c_m)^3 \tag{3}$$

as shown by Figure 6.

The pure  $F$  suspensions did not display any change of arrival time with time elapsed after stirring while the apparatus was being filled. Apparently they set immediately. The  $F$  suspensions to which small amounts of salt were added had so little gel strength that no transmitted pulse could be detected. However, after addition of the flocculating amount of 60 meq/liter NaCl a slowly setting gel was obtained, as reflected by a decrease of arrival time of the pulse as setting time increased. The modulus of elasticity appears to increase exponentially with the setting time (Fig. 7). With higher salt concentration the gels become more rigid and set a little more rapidly.

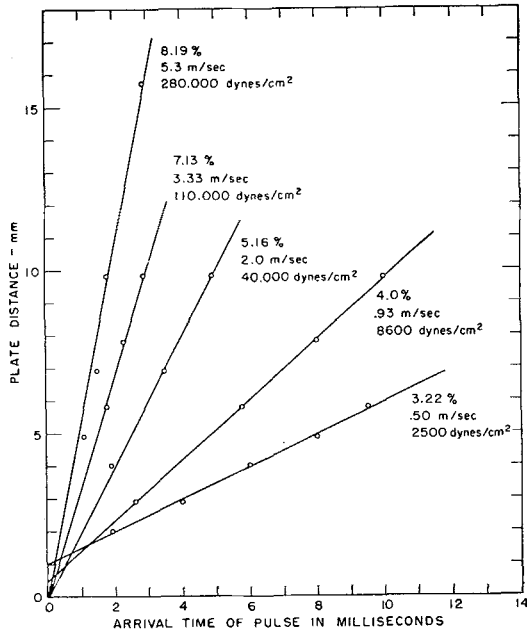


FIGURE 5.—Arrival time of pulse at different plate separations for five different concentrations of  $F$  suspensions.

Apparently the salt-containing gels show a marked thixotropic hysteresis, which is absent in pure gels. This difference in character of the two types of gels has been observed earlier (van Olphen, 1951a) by measuring the yield stress of the two gels as a function of setting time, in the modified Stormer viscometer. The pulse shearometer is a more elegant tool for studying thixotropy because the system is not disturbed by the measurements at different setting times.

#### *Dilute Suspensions*

*Ostwald capillary viscometer.*—The relative viscosity of dilute suspensions, showing Newtonian behavior, was determined with an Ostwald capillary viscometer. Such measurements have been reported before (van Olphen, 1954) and here the results are given for the presently used  $F$  suspension. In Figure 8 the relative viscosity is plotted versus the suspension concentration, and the plot is linear in the range of concentrations used. The rather high relative viscosity values can be explained by the anisometry of the particles and the data can actually be used to determine the axis ratio of the particles.

The effect of NaCl on the relative viscosity of an  $F$  suspension 0.25 percent by weight is included in Figure 8. The decrease of the relative viscosity and its subsequent rise on salt addition (which was observed earlier) is very analogous to the change of the Bingham yield stress of more concentrated suspensions, though less pronounced.

## SEDIMENTATION BEHAVIOR

*Sediment Volume in the Ultracentrifuge*

The sediment volume of 100-ml portions of a *T* suspension 2.17 percent by weight were measured as a function of the amount of NaCl added after spinning in the ultracentrifuge ("Spinco," preparative). One run was made for 960 minutes at 7500 rpm (average 6000 g) and another run for 120 minutes at 15,000 rpm (average 22,000 g).

NOTE: In the supernatant liquid the amount of clay that did not settle under the conditions of the test was determined gravimetrically (correcting for the amount of salt present). The sediment volumes were corrected accordingly. This correction was never higher than 5 percent and decreased with increasing salt concentrations; the corrections did not alter the general shape of the curves.

The results are shown in Figure 9, in which the sediment volumes are plotted as a function of the salt concentration for the two runs. At the lower speed the sediment volume decreases sharply with the addition of small amounts of salt but increases again with additional salt, analogous with the yield stress behavior reported above. At the higher speed, the large centrifugal force tends to flatten the curve after the first sharp drop of sediment volume at low salt concentrations, and the minimum disappears. Apparently the salt-containing gels collapse under these forces, whereas the collapse of the pure gel is very slight.

*Filter Cake Thickness*

The same suspensions used for the sediment volume determinations were submitted to a normal API filtration test with ultrafine filters. The thickness of the

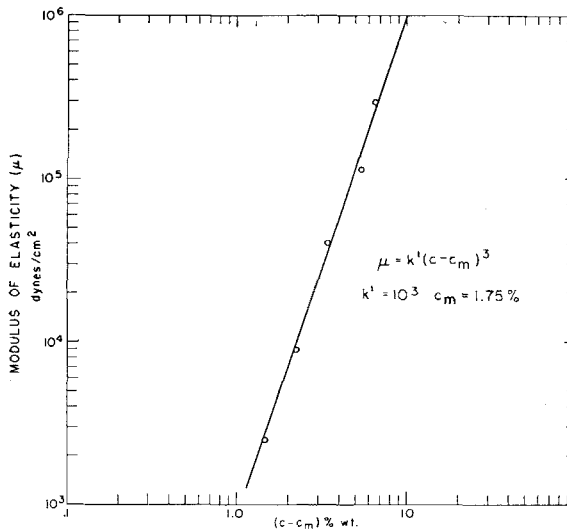


FIGURE 6. — Modulus of elasticity of *F* suspensions as a function of  $(c - c_m)$ .

filter cake after 30 minutes filtration was measured by weighing the cake plus filter, both in air and under water. The density of the cake was also calculated from these figures, and results are included in Figure 9. The curve has the same general shape as that for the sediment volume at low gravitational fields.

DISCUSSION OF RESULTS

*Effect of Salt Addition on the Rheological and Sedimentation Behavior*

Attention may be drawn to the peculiar effects of NaCl on the rheological and sedimentation properties of the bentonite gels.

In the effect of salt additions there is a definite parallelism among the Bingham yield stresses, the sediment volume, and the filter-cake thickness and its specific volume. All decrease sharply with the addition of small amounts of salt, but increase after larger salt additions. All three properties reach minimum values at salt additions in the range of 2 to 10 meq/liter NaCl. Such a parallelism is to be expected from general colloid chemical experience (see for example Verwey and Overbeek, 1948, p. 15, and Eggleton and Puddington, 1954).

From a colloid chemical point of view it seems puzzling, however, that the pure system is obviously in the flocculated state and deflocculates on addition of small amounts of salt. The subsequent rise of the yield stress on further addition of salt, on the other hand, can be considered the normal consequence of the flocculating action of NaCl.

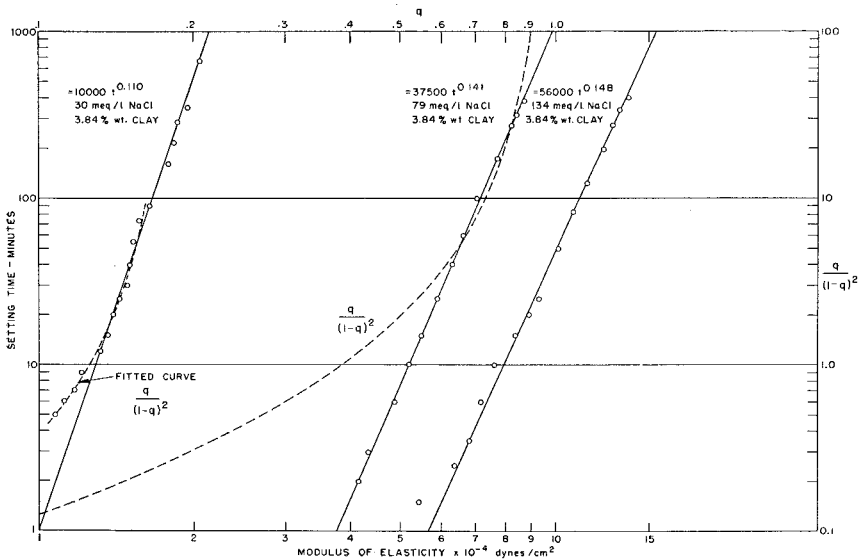


FIGURE 7. — Modulus of elasticity as a function of setting time for *F* suspensions with various amounts of NaCl added.



In general, highly purified colloidal systems may be in the flocculated state because of the lack of a peptizing electrolyte. For example, small quantities of KI or  $\text{AgNO}_3$  are required to bring a pure silver iodide suspension to the peptized state. Either  $\text{Ag}^+$  or  $\text{I}^-$  is a potential determining ion for AgI. Therefore, one might think that NaCl, added in small quantities to bentonite, acts as a peptizing electrolyte. However, a more detailed consideration of the structure of the electrical double layers on the various surfaces of the bentonite particles reveals that such a peptizing action of NaCl is unlikely. The flat double layer originates from a lattice charge deficiency due to isomorphous replacements of higher-valent cations by lower-valent ones. The (exchangeable) sodium ions that compensate this charge deficiency are already present in the dry clay, and in contact with water an electrical double layer of the constant-charge type is formed. Moreover, any change in the degree of flat surface association would not be expected to have such large bulk rheological effects as those reported above. The other part of the clay particle, the edge surface, will carry an electrical double layer which is analogous to that of aluminum hydroxide sols as pointed out earlier (van Olphen, 1950a). For such sols NaCl does not act as a peptizing electrolyte.

In earlier work (van Olphen, 1951, 1951a) an alternative explanation was based on the hypothesis that, although the flat double layers are undoubtedly negative, the edge double layers may carry a positive double layer, as do aluminum hydroxide particles. Then the state of agglomeration of the pure suspension may be seen as an internal mutual flocculation by edge-to-flat-surface association. Upon addition of a little salt both double layers will be compressed, shifting part of the counter ions to the Stern layer and reducing the effective surface charge. The mutual attraction will be reduced, and deflocculation will result. More salt then causes normal flocculation, owing to predominating van der Waals attractive forces; edge-to-edge as well as edge-to-flat-surface and flat-

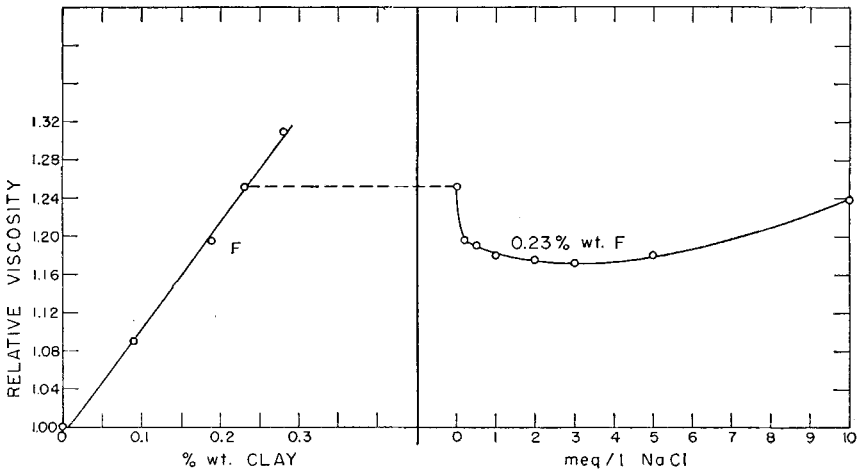


FIGURE 8.—Relative viscosity of dilute *F* suspensions as a function of clay concentration and the amount of NaCl added.

surface-to-flat-surface association can then take place, again resulting in structure formation and yield-stress development.

It has been emphasized that the characters of the gels in the two regions of gelation are quite different. The pure gels show no thixotropic hysteresis: after stirring is discontinued they set immediately, whereas the salt-contaminated flocculated systems set slowly after stirring. It will be shown later that this difference in behavior can be explained by the postulated difference of the mechanism of gelation.

*Rheology and Particle Linking Forces in Bentonite Gels*

*Gel development.*—Dilute suspensions of bentonite behave as Newtonian liquids. The rather high relative viscosity of these suspensions can be explained as a consequence of the anisometry of the particles. When the clay plates are idealized as flat ellipsoids of revolution an axis ratio of 460 is computed from the relative viscosity data (van Olphen, 1951, p. 42, 81, 82). Assuming a thickness of 17 Å for the dry micelle, a diameter of about 8000 Å is computed for the particles of the *F* suspension.

With increasing clay concentration, particle attraction will cause deviation from Newtonian behavior as shown by the development of elasticity and a yield stress. The particles will arrange in a scaffolding structure, linked in the position of a minimum in the attractive potential curve.

There has always been some question whether yield-stress development in these systems is actually caused by particle linking. An alternative explanation known as the lysosphere theory has been proposed, in which the rigidity is ex-

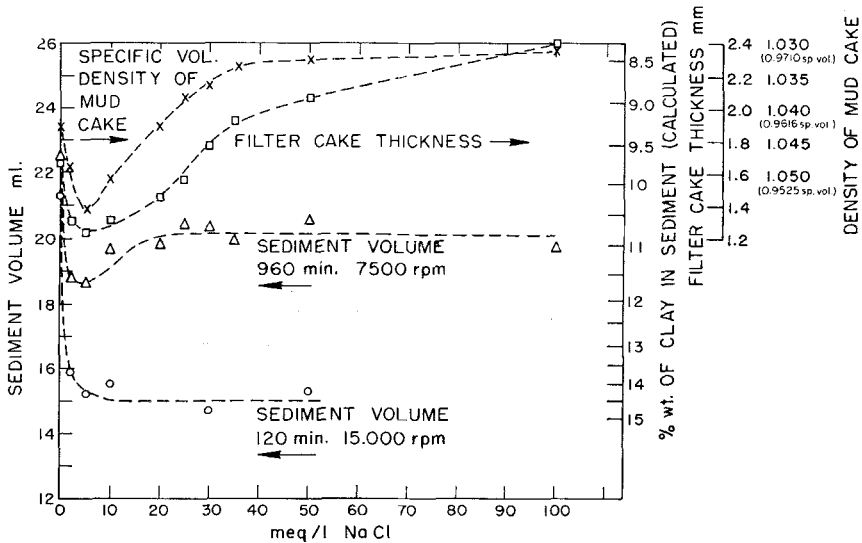


FIGURE 9. — Sediment volume and filter-cake thickness of 2.17 percent (by weight) *T* suspension as a function of NaCl concentration.

plained by the close packing of strongly hydrated particles. In our case, where gels are developed at rather low clay concentration, the lysosphere theory would require an extremely far-reaching hydration effect for which there is no theoretical basis. On the other hand, because of the extreme anisometry of the particles, a scaffolding structure can be visualized at very low concentrations. An ideal cubic network with plate contact can be constructed for plates  $10^4$  by  $10^4$  Å, 2 unit layers thick, at a clay concentration as low as 1.6 percent by weight. The first measurable yield stress in our  $F$  suspension actually occurs at such a low clay concentration. With the  $T$  fraction a slightly higher minimum concentration is required. This must be due to a larger average thickness of the clay plates. If the plates were larger only in length or breadth and not thicker, less clay would be required to develop a gel. That the larger plates are really thicker is borne out by the data of Kahn and Lewis (1954) on electro-optical birefringence of a number of bentonite fractions.

Recently, a proof of particle contact in clay gels was claimed by Hofmann and others (Weiss, Fahn, and Hofmann, 1952; Fahn, Weiss, and Hofmann, 1953; Call, 1953). Aerogels were made from a bentonite hydrogel by freeze drying, in which the original structure of the hydrogel is thought to be undisturbed since the pores are not collapsed by the receding meniscus as is the case in the normal drying of a gel. The aerogels had indeed good coherence and practically the same volume as the hydrogel. We repeated the experiments and found that not only could an aerogel be obtained from one of our pure gels but also from a system containing 5 meq/liter NaCl, which in the hydrous form has practically no gel strength. As was also observed by Hofmann the aerogel has rather large visible pores and slits. The nitrogen surface area of the aerogels determined by C. S. Brooks of this laboratory appeared to be the same as that of a normally dried bentonite for the pure gel ( $27.2\text{ m}^2/\text{gm}$ ), and for the gel with 5 meq/liter NaCl, even smaller ( $4.4\text{ m}^2/\text{gm}$ ). This indicates that in the aerogels the average degree of unit layer association per particle is 50 and 180, respectively. It seems unlikely, in connection with particle size determinations, that such a high degree of layer association occurred in the hydrogels. All these observations suggest that secondary changes have taken place in the gels during the freeze-drying process. Therefore, these experiments do not supply the definite proof of particle contact in the hydrogels.

*Bingham yield stress as a function of clay concentration.*— After the clay concentration has reached the point at which a coherent network is built up throughout the system, the Bingham yield stress rises rapidly with increasing clay concentration. It seemed worth while to try to write the dependence of yield stress on clay concentration as a bimolecular reaction analogous to Smoluchowski's flocculation theory.

The data could be fitted in the form:

$$\tau_B = k(c - c_m)^2.$$

As represented by Figure 3, the  $c_m$  values found for the  $T$  suspension and the  $F$  suspension with or without salt are very close to the values of the clay concentrations at which the yield stress is first developed. The relation is valid for clay concentrations which are more than about 0.5 percent above the critical concentration. The significance of this relation will be discussed in more detail later.

*Elastic behavior.*— At small amounts of shear the gels are seemingly perfectly elastic. At least for the pure gels which do not show thixotropic hysteresis the arrival time of the pulse does not change upon repetitions of the pulse on the same sample or when the amplitude of the pulse is varied.

The modulus of elasticity rises more rapidly than the Bingham yield stress with  $(c - c_m)$ , viz., with the third power instead of the second:

$$\mu = k'(c - c_m)^3 \quad (3)$$

During elastic deformation many links will probably act only as hinges and only a fraction of the links will be deformed and contribute to the elastic stress. This fraction of links actually contributing to the stress seems to increase rather rapidly with clay concentrations.

*Effect of shear rate.* — The bentonite suspensions behave very much as Bingham plastics. An analysis of Bingham behavior proposed by Goodeve (1939; 1948) is reviewed briefly here.

The well-known equation for Bingham flow is

$$\tau - \tau_B = n_{\text{diff}} j \quad \text{or} \quad \tau = n_{\text{diff}} j + \tau_B. \quad (4)$$

The second form of the equation indicates that the shearing force  $\tau$  is composed of two contributions, one a normal viscosity contribution which is linearly dependent on the shear rate  $j$  ( $n_{\text{diff}}$  is the “differential viscosity”), and the other,  $\tau_B$ , the “Bingham yield stress” which is independent of the shear rate. Apparently two different mechanisms are responsible for the two contributions.

Presenting the formula a little differently, one can introduce an apparent viscosity defined as  $\tau/j$  and write (4) as follows:

$$\eta_{\text{apparent}} = n_{\text{diff}} + \tau_B/j, \quad (5)$$

so that the differential viscosity may be considered the residual viscosity at infinite shear rates.

Goodeve's theory for the explanation of a shear independent contribution to the force for linked scaffolding structures is as follows:

When the particle structure is sheared the particles are stretched by the deformation, because the links pull at the particles. In the particles an elastic force develops and the stretching procedure goes on until the elastic force within the particles exceeds the linking force between them. As the particles are stretched up to the point at which the link breaks, an impulse is given from the shearing plane to the reference plane. Longer time is required to reach the critical elongation at low shear rates than at high rates; therefore the magnitude of the impulse will be inversely proportional to the rate of shear. The total force between the planes is obtained by multiplying the average value of an impulse by the number of impulses per second per  $\text{cm}^2$ . This rate of impulses will be proportional to the rate of shear and therefore the product of impulse and rate or the total force will be independent of shear rate.

Goodeve (1948) elegantly demonstrated this mechanism by means of a simple mechanical model. A disc with radially mounted brushes is rotated. The brushes engage in turn with a single brush and the force on this brush can be measured. The force on the single brush appears to be independent of the rate of rotation of the disc with brushes.

Mathematically the mechanism can be treated as follows:

Consider a particle which moves in the shearing plane and which is linked to another particle in a reference plane as sketched in Figure 10.

The distance of the shearing plane from the reference plane is of the order of the dimension of the particle ( $z$ ). At a shear rate  $j$  the particles will be stretched a distance  $x = jzt$  in the time  $t$  (Fig. 10).

Assuming, for example, that the stretching force increases proportionally with the extension according to Hooke's law, an elastic force  $f = Hx = Hjzt$  is developed at the time  $t$ .

If  $x_c$  is the critical extension of the particle at which the elastic force  $f_c$  exceeds the force of the link, it will take  $t_c = f_c/Hzj$  seconds to break the link.

Then the impulse given to the reference plane will be

$$\int_0^{t_c} f dt = \frac{1}{2} \frac{f_c^2}{Hzj}$$

which shows that the impulse is inversely proportional to the rate of shear  $j$ .

If  $n_i$  is the instantaneous number of links per cc the number of impulses per second per  $\text{cm}^2$  is equal to  $n_i z / t_c$  or  $n_i z^2 H j / f_c$  which is proportional to  $j$ .

Finally the total force is

$$F = \tau_B = \frac{1}{2} f_c n_i z \tag{6}$$

This force is therefore independent of the rate of shear if  $n_i$ , the instantaneous number of links, is independent of the rate of shear. The latter is valid only when thermal making and breaking of links is assumed to be negligible as compared with shear making and breaking. Then, the rate of shear breaking is

$$\frac{dn_i}{dt} = - \frac{n_i}{t_c} = - \frac{n H z j}{f_c} \tag{7}$$

The rate of shear making can be derived as in Smoluchowski's collision theory in colloidal suspensions (Kruyt, 1952, p. 290-291). The rate of disappearance of particles by collision to form duplets caused by shear in the absence of any energy barrier is found to be

$$\frac{dN}{dt} = \frac{4}{3} z^3 (N_o - N)^2 j \tag{8}$$

where  $N_o$  is the total number of particles,  $N$  the number of linked particles, and  $z$  the radius of collision.

With every two particles considered potential partners to a link,  $N_o = 2n_o$  and  $N = 2n_i$ ; and then equation (8) can be written:

$$\frac{dn_i}{dt} = \frac{2}{3} z^3 (2n_o - 2n_i)^2 j . \tag{8a}$$

In the steady state of shear:

$$\frac{dn_i}{dt} = - \frac{n_i H z j}{f_c} + \frac{2}{3} z^3 (2n_o - 2n_i)^2 j$$

which is equal to zero, and thus  $n_i$  is a constant independent of shear.

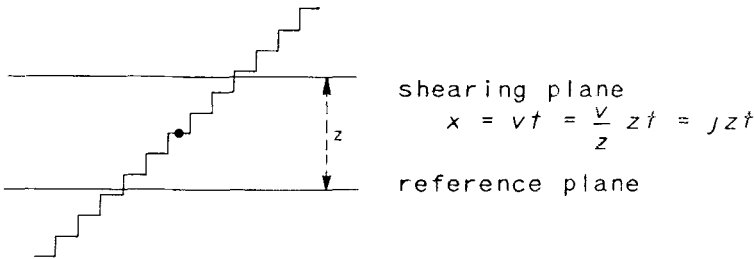


FIGURE 10. — Illustration of Goodeve's treatment of Bingham flow.

It also follows from the last equation that  $n_i$  is proportional to  $(n_o - n_i)^2$ . At the same time  $n_i$  is proportional to  $\tau_B$  (6) and since beyond the minimum concentration to obtain a gel,  $c_m$ , the Bingham yield stress is proportional to  $(c - c_m)^2$ , the corrected concentration  $(c - c_m)$  will be proportional to  $(n_o - n_i)^{1/2}$ . If the number of potential partners to a link and thus the number of potential links is considered to be proportional to  $(c - c_m)$ , it follows that  $n_i$  must be small compared with  $n_o$ . This is indeed shown from the calculations in the section on evaluation of the linking force between the particles of the pure gels and the shearing mechanism.

### PARTICLE LINKING FORCES: A SEMIQUANTITATIVE EVALUATION

Since the bentonite gels follow the Bingham flow behavior at shear rates of the order of  $100 \text{ sec}^{-1}$  and higher, the shear making and shear breaking of the links predominates in this region: It is the shear, not the thermal energy, which determines the life of a link. Apparently the energy of the links in both the pure gels and the salt-flocculated gels is high with respect to  $kT$ .

The main difference between the two types of gel is that the pure gels are not thixotropic, whereas the salt-flocculated gels are. From this it may be concluded that there is an energy barrier for flocculation in the salt-containing gels and no such barrier in the pure gels. This is in line with the postulated difference between the two types of gel: In the pure gels there is supposed to be positive-edge to negative-surface association, for which there would be no energy barrier; in the salt-flocculated gels the particle association is governed by a potential curve which is the summation of the remaining double-layer repulsion and the van der Waals attraction. At moderate salt concentrations there may be expected to exist a maximum in the net potential curve as shown by Verwey and Overbeek (1948). This maximum is the energy barrier which retards flocculation. Thus the pure gels are a result of rapid coagulation; the salt-containing gels come about by slow coagulation.

It seems worth while to obtain quantitative estimates of both the linking force between the particles and the height of the energy barrier from the collected rheological information. Actually, the rheological behavior of the concentrated suspensions seems to be the most direct tool for evaluation of such data.

*Evaluation of the linking force between the particles of the pure gels and the shearing mechanism.* — The following three requirements must be fulfilled and from them the linking force can be evaluated:

1) The shearing force must be able to concentrate sufficient force on a link to break it, thus  $f_j > f_c$ . The possibility should be considered that the shear can break only a single link between an assembly of particles having a width of  $p$  times the width of a single particle.

2) The number of instantaneous links between assemblies of particles,  $n_i$ , must be smaller than the number of potential partners to a link  $n_o$ .

3) Since the Bingham flow behavior is followed by the pure gels beyond a rate of shear of the order of  $100 \text{ sec}^{-1}$ , the time  $t_c$  to break a link by a shear beyond this shear rate must be smaller than the average kinetic life of a link,  $t_k$ .

<sup>1</sup> Although the analogy of proportionality with either  $(n_o - n_i)^2$  or  $(c - c_m)^2$  may be misleading,  $c_m$  is in no way connected with  $n_i$ .

Thus  $t_c < t_k$  for  $j > 100 \text{ sec}^{-1}$ , and  $t_c$  and  $t_k$  become of the same order for  $j = 100 \text{ sec}^{-1}$ .

From these requirements  $p$  and  $f_c$  may be evaluated, using the data for  $\tau_B$  at different clay concentrations. The result of the calculation, given below, is that  $p$  is of the order of 10 and  $f_c = 10^{-4}$  dyne, the interaction energy being of the order of  $15 kT$ .

For the calculations we take the following data, mentioned earlier:

Case	$c$ % wt	$(c - c_m)$ % wt	$\tau_B$ dn/cm <sup>2</sup>	$j$ sec <sup>-1</sup>	$\eta$ poises	$\mu$ dn/cm <sup>2</sup>
I	2.41	0.66	45	100	0.2	
II	3.22	1.47	200	100	0.5	2,500
III	4.10	2.35	500	100	1.0	10,000

The first requirement is that  $f_j > f_c$  or  $6\pi\eta \left[ \frac{pz}{2} \right] v > f_c$  or  $6\pi\eta \left[ \frac{pz}{2} \right] jpz > f_c$  which gives:

$$\text{I: } f < 188 z^2 p^2 \quad \text{II: } f_c < 470 z^2 p^2 \quad \text{III: } f_c < 940 z^2 p^2$$

The second requirement is  $n_i < n_o$  or

$$n_i = \frac{2\tau_B}{pzf_c} < \frac{1}{2} \frac{0.01 (c - c_m)}{2 \times 9.4 \times 10^{-8} \times 2.70 \times p^2 z^2}$$

where 2 is the assumed number of layers in a particle,  $9.4 \times 10^{-8}$  the thickness of a layer in a dry particle, and 2.70 the density of the dry clay; from which it follows that

$$\text{I: } f_c > 1.38 \times 10^{-2} zp \quad \text{II: } f_c > 2.75 \times 10^{-2} zp \quad \text{III: } f_c > 4.32 \times 10^{-2} zp .$$

The third requirement is that  $t_c < t_k$  or (Goodeve, 1939, p. 351, eq. 8):

$$\frac{px_c}{pzj} < \frac{1}{v} e^{\frac{1}{2} x_c f_c / kT}$$

since the work required to break the link is equal to the work done to stretch the particles, which is

$$\int_0^{x_c} f dx = \int_0^{x_c} H x dx = \frac{1}{2} f_c x_c .$$

It appears reasonable to take  $x_c = 10^{-8}$  cm for the critical extension and  $v = 10^{12}$ , according to Goodeve (1939, p. 353) thus:

$$\frac{1}{z} < 10^{-2} e^{1.25 \times 10^5} f_c .$$

In the following table the limits obtained from the first two requirements are given for some chosen values of  $pz$ . It was assumed that  $f_c$  and  $pz$  are independent of the clay concentrations so that the limits are narrowed to  $f_c < 188 (pz)^2$  and  $f_c > 4.32 \times 10^{-2} pz$ .

When	$pz = 5 \times 10^{-4}$	then	$4.7 \times 10^{-5} > f_c > 2.15 \times 10^{-5}$
	6		6.75
	7		9.2
	8		12.0
	9		15.2
	10		18.8

From the third requirement it is found that  $f_c = 1.12 \times 10^{-4}$  dyne if for  $j = 100 \text{ sec}^{-1}$ ,  $t_c$  and  $t_{ic}$  are assumed to be equal. Thus at a shear rate of  $100 \text{ sec}^{-1}$  the shearing force can break such a link when it can act on an assembly of particles with a width of  $8 \times 10^{-4}$ . As a single particle has a diameter of  $8 \times 10^{-5} \text{ cm}$  the value of  $p$  is about 10. The energy of the link is

$$\frac{1.12 \times 10^{-4} \times 10^{-8} \times \frac{1}{2}}{0.4 \times 10^{-13}} kT = 15kt.$$

Finally the number of instantaneous links can be computed for the three cases and compared with the number of potential partners to a link,  $n_o$ . The following results are obtained:

Case	For assemblies of diameter $pz$	
	$n_i$	$n_o$
I	$1.8 \times 10^9$	$1.0 \times 10^{10}$
II	$8.0 \times 10^9$	$2.25 \times 10^{10}$
III	$2.0 \times 10^{10}$	$3.6 \times 10^{10}$

In order to evaluate the number of links,  $n_{es}$  that contribute to elasticity, equation (8a) must be modified somewhat since it was found that shear breaks only links between larger units rather than between the individual particles. However, in the range of elastic deformations also the links between the individual particles in the assemblies of particles must be taken into account.

Shear breaking is given by:

$$\frac{dn_i}{dt} = -\frac{n_i}{t_c} = -\frac{n_i H p z j}{f_c}$$

where  $n_i$  is the number of instantaneous links between assemblies of particles.

Again shear making can be derived from Smoluchowski's theory of coagulation under shear as follows:

The rate of disappearance of primary particles is  $dv/dt = 4/3 z^3 v^2$ , where  $v$  is the number of particles at a given time and  $z$  the radius of collision of these primary particles;  $v = v_o - v_t$  where  $v_o$  is the original number of primary particles and  $v_t$  the number of linked particles at a given time;  $v_t = 2pn_i$  and thus  $dv/dt = 2p \, dn_i/dt$ . Further  $v_o = 2n_o^*$  the number of possible links between primary particles. Equation (8a) now becomes:



$$\frac{dn_i}{dt} = -\frac{n_i H z p j}{f_c} + \frac{4}{3} \frac{z^3}{2p} (2n_o^* - 2pn_i)^2 j = 0. \quad (8b)$$

$H$  may be found from the modulus of elasticity by using the relation that the total stress developed in the elastic region is:

$$\tau = \mu \frac{x}{z} = n_o z f = n_o z H x \text{ or } H = \frac{\mu}{n_o z^2}$$

where  $n_o$  is the number of links contributing to elasticity.

Substituting the expression for  $H$  and that for  $n_i = 2\tau_B/pzf_c$  in equation (8b) the following values for  $n_o$  are found for the examples II and III for which the modulus of elasticity was measured. The data are compared with the total number of possible links in a continuous structure  $2n_o^*$ .

Case	$n_o$	$2n_o^*$	Percentage of $2n_o^*$
II	$0.63 \times 10^{11}$	$5.5 \times 10^{12}$	1.4
III	$2.45 \times 10^{11}$	$7.2 \times 10^{12}$	3.4

Since  $\tau_B$  was found to be proportional to  $(c - c_m)^2$  the number of instantaneous links would be expected to be small compared with the number of possible links. Thus, in equation (8b)  $2pn_i$  should be small compared with  $2n_o^*$ . The following table shows that this is indeed the case:

Case	$2pn_i$	$2n_o^*$	Percentage of $2n_o^*$
I	$3.6 \times 10^{10}$	$2.0 \times 10^{12}$	1.8
II	$1.6 \times 10^{11}$	$4.5 \times 10^{12}$	3.5
III	$4.0 \times 10^{11}$	$7.2 \times 10^{12}$	5.5

A few words may be added about the effect of shear rate on  $n_i$ . From equation (8a) it was inferred that  $n_i$  would be independent of shear rate. There it was assumed, however, that  $z$  would be a constant, but from the result that links can be broken only if the shear can act on an assembly of particles, it may be expected that with increasing shear rates links between smaller assemblies can be broken and thus  $z$  or  $p$  may decrease in proportion to the square root of the shear rate. Since over a range of shear rates  $\tau_B$  was found to be constant, the product  $n_i z p$  must be constant. Apparently  $n_i$  increases in proportion to the square root of the shear rate. These changes of  $n_i$  are rather small since they would amount to a factor  $\sqrt{3}$  in the range of shear rates from 100 to 300  $\text{sec}^{-1}$  where strict linearity is observed (Fig. 1).

*Evaluation of the height of the energy barrier in the NaCl-flocculated gels from the thixotropic increase of the modulus of elasticity.*—The thixotropic increase of the modulus of elasticity of a gel with time is a consequence of the increase of the number of links with time after these links have been broken by previous shear. The phenomenon is analogous to the slow coagulation of dilute sols on addition of electrolyte. For dilute systems the coagulation theories of Smoluchowski and Fuchs have been checked by particle counting or by indirect means of particle-size determinations. To our knowledge the theory has never been applied to data on the thixotropic stiffening of gels and it seems worth while to try this.

It will be assumed that in the process of setting the gel only thermal making of links takes place and no thermal breaking, for the following reason: When the particles upon mutual approach pass the barrier, they will occupy the position of the rather deep van der Waals energy minimum. The difference between this minimum and the barrier will be too great to allow the particles to be disengaged thermally to any practical extent.

The rate of thermal making of links in Fuchs' theory (Kruyt, 1952, p. 283-285) in the presence of an energy barrier  $E$  is given by:

$$\frac{dn}{dt} = 4\pi Dz (2n_o^* - 2n^*)^2 e^{-E/kT} \tag{9}$$

where  $2n_o^*$  is the number of possible links between primary particles, and  $2n^*$  the number of links formed between those particles in a continuous structure.  $D$  is the diffusion constant.

The modulus of elasticity can be written  $\mu = n_e H z^2$  and it is found experimentally that  $\mu = \mu_1 t^a$ . Thus

$$\frac{d\mu}{dt} = \mu_1 a t^{(a-1)} = H z^2 \frac{dn_e}{dt} \tag{10}$$

$E$  can be determined if the two equations (9) and (10) can be combined. Therefore  $n_e$  and  $n^*$  must be related. In the pure systems the modulus of elasticity was observed to increase with the third power of the number of possible links, and the yield stress with only the square of this number; therefore  $n_e$  would grow with the power  $1\frac{1}{2}$  of  $n^*$ . Assuming that the same holds for the salt-flocculated systems we may write:

$$n_e = C n^{\frac{1}{2}} \text{ or in general } n = C n^* \text{ or } \frac{dn_e}{dt} = C b n^{b-1} \frac{dn^*}{dt} \tag{11}$$

From (10) and (11) it is found that  $dn^*/dt = n^* a/bt$ . Substituting this in equation (9) and writing  $D = kT/6\pi\eta z$  gives the following expression:

$$e^{E/kT} = 2.67 \frac{kTb}{na} \frac{(n_o^* - n^*)^2}{n^*} t \tag{12}$$

If we write  $n^*$  as a fraction  $q$  of  $n_o^*$ , this fraction can be evaluated from the experimental results by the method of curve fitting. In Figure 6 the curve representing  $q/(1 - q)^2$  versus  $q$  must be fitted on the experimental curve for the relation between  $t$  and the modulus of elasticity. This fit is shown for the data for 30 meq/liter NaCl. From the fit of the curves it is derived that at a time of 10 minutes the value of  $q$  is 0.68 (Fig. 6).

The following numerical data can now be put into equation (12):  $c = 3.84$  percent,  $c_m = 1.00$  percent,  $c - c_m = 2.84$  percent. Then

$$n_o^* = \frac{1}{2} \frac{0.01(c - c_m)}{2 \times 9.4 \times 10^{-8} \times 2.70 \times (8 \times 10^{-5})^2} = 4.35 \times 10^{12}$$

$$n^* = 0.68 \times n_o^* = 3.0 \times 10^{12}$$

$kT = 0.4 \times 10^{-13}$  erg,  $\eta = 0.5$  poise,  $b = 1\frac{1}{2}$ ,  $a = 0.110$ ,  $t = 600$  sec. The result is that  $e^{E/kT} = 1150$ , or  $E = 7kT$ .

This seems a reasonable order of magnitude for a slowly coagulating system which would require an energy barrier of the order of  $20kT$  for almost permanent stability at the given concentration.

The fit of the theoretical and the experimental curves is limited to the lower range of times. With increasing time  $\log \mu$  continues to grow proportionally to  $\log t$  whereas the theoretical curve bends to a saturation value for  $\mu$ . Probably in the course of the process an increasing amount of cross linking takes place amounting to more than one link per particle so that  $2n_0^*$  increases during the process.

For the other salt concentration the curvature in the first stages of the experiment was missed. In these rigid gels the breakdown of the structure by stirring is difficult to achieve. Therefore there is no possible way of locating a fitting curve in these experiments.

The number of links contributing to elasticity  $n_e$  cannot be computed in these systems. However, at a time of 10 minutes the system treated with 30 meq/liter of NaCl shows a modulus of elasticity of the order of  $10^4$ . In the pure gels this modulus of elasticity was observed at a concentration of links contributing to elasticity of  $2.5 \times 10^{11}$ . Therefore, if the mechanism of deformation in the salt-flocculated gels is the same as that in the pure gels it may be concluded that in the former about 5 percent of the actual links  $2n^*$  contribute to elasticity.

At comparable clay concentrations the modulus of elasticity in the salt-treated gels becomes much higher than that in the pure gels. This would indicate that owing to the increased cross linking in the salt-containing gels relatively fewer links can act as hinges. The development of more cross linking in the salt-flocculated gels is in line with the working hypothesis that in these gels both edge-to-edge and edge-to-flat-surface association can occur, whereas in the pure gels only the latter association is supposed to take place.

In conclusion it should be emphasized that these computations have a rather approximate character. Refinements may be made by postulating more detailed models of the gel structure and their modes of deformation, which are, however, still rather speculative. For example, in analyzing the forces involved in Bingham flow, one could assume that the particles tend to orient to some degree, making an angle with the flowlines up to 45 degrees. This would involve factors of the order of  $\sqrt{2}$ , however, and would not change the orders of magnitude in the result.

Possibly conductivity measurements may supply additional information on the structure and deformation of the gels, as was shown by Bondi (1953) for carbon-black suspensions. The effect of temperature on Bingham flow and on thixotropic setting might also be profitably studied.

The purpose of the computations was to show how semiquantitative estimates of particle interaction energies can be gained from such a direct tool as rheological measurements. In our opinion it is encouraging that, without going into considerable detail, reasonable orders of magnitude for the interaction energies are obtained.

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#### Author's note

Dr. E. A. Hauser (1956) published a criticism of the foregoing paper in a review of the Clay Conference in the *Kolloid Zeitschrift*. The following is a reply to his criticism.

That "the author claimed that the minimum concentration of a bentonite sol which would give a thixotropic system was well over 3%" is a wrong quotation. The paper only shows that the minimum clay concentration at which a Bingham system develops, according to the lowest measured Bingham yield stress of about 5 dynes/cm<sup>2</sup>, is between 1 and 2½ percent for sodium bentonite suspensions, depending on the size fraction and the electrolyte content.

Then Dr. Hauser remarks: "In the discussion which followed his presentation he [van Olphen] was told that a thixotropic gel could be obtained already at a concentration of 0.05% clay." There is certainly no doubt that particle interaction makes itself felt at lower clay concentrations than 1 percent. There are many indications of some structure formation in dilute clay suspensions when treated with electrolytes. This is not surprising if one considers the size and shape of the clay particles: if one would line up all the particles in 100 ml of a 0.01 percent sodium-bentonite suspension a ribbon of a length of about a thousand miles would be obtained. Weakly linked networks can certainly be formed in these suspensions and their disturbance and recovery would give phenomena which are analogous to thixotropy. My paper, however, did not deal with these extremely dilute salt-containing systems which Dr. Hauser called thixotropic sols rather than thixotropic gels in his paper (Hauser, 1929).

The criticism continues: "He was also told that thixotropy has nothing to do with coagulation at all and that a survey by him of the literature available might be advisable before making such statements as he did." This statement is contrary to most concepts on thixotropy which are found in the modern literature. (For a discussion see Verwey and Overbeek, 1948, p. 10-11, and Kruyt, 1952, p. 363-366). Dr. Hauser's remark is probably the result of a disagreement on terminology: Gelation of inorganic hydrosols on electrolyte addition which is frequently shown by those sols containing anisodimensional particles is seen as an initial stage of flocculation (the Schulze-Hardy rule applies). Preponderant particle attraction leads to particle fixation in a framework. When such a framework is disturbed by shear, its thixotropic recovery is analogous to slow coagulation. Also Dr. Hauser has concluded that network formation occurs in these systems. His (Hauser and Reed, 1937) classical studies on thixotropy should be referred to, in which it is concluded:

"Ultramicroscopic observation indicates that gelation consists in the formation of primary

clusters of individual particles, followed by secondary aggregation of these clusters into a network intermeshed with channels and patches of free dispersion medium."

This is certainly what can be described as a form of coagulation.

The next remark that the paper was "based . . . on mathematics, rather than on experimental facts" is taken care of by the experimental material which is presented in the paper.

Finally the statement that the author "seemingly also did not realize that the type of counter ions present in bentonites must be taken into serious consideration" must be denied. The work presented was done on mono-ionic sodium bentonite and it was mentioned in the verbal presentation that at present work on calcium bentonite is in progress.

So much for the reply to Dr. Hauser's criticism. The following remarks about the various mechanisms of gelatin and thixotropy, however, might be added [see also the discussion by Hauser and Reed (1937) and by Alexander and Johnson (1949, p. 610) and Hofmann (1952)]:

Except for the now obsolete picture of long range hydration, all pictures agree on some type of network formation by attractive, that is, coagulating particle interaction forces. However, three still different types of particle interaction may be distinguished:

(i) Attraction between a positive double layer on clay edges and a negative double layer on the flat surfaces. This mechanism was postulated in our work for the pure sodium-bentonite gels. The absence of an energy barrier in this system would explain its nonthixotropic character.

(ii) Predominating van der Waals attraction due to compression of the electrical double layer by electrolyte which reduces the range of the electrical repulsive forces. At moderate electrolyte concentration a small energy barrier remains which causes a slow recovery of the structure after disturbance by shear. This concept was applied to the salt-containing bentonite gels which show thixotropic hysteresis.

(iii) Anisodimensional particles may be fixed in a parallel position at a considerable distance owing to a secondary minimum in the potential curve. (Verwey and Overbeek, 1948, p. 12, 13, 124, 125, 184). This picture is often used to explain such phenomena as tactoid formation, Schiller layers and also thixotropy. This picture has not been applied in my paper since it could not explain the remarkable sequence of nonthixotropic gelation, breakdown of the gel, and thixotropic gelation on addition of increasing amounts of salt to the pure gels. Also other studies, particularly those on the effects of small amounts of specific anions on the yield stress of bentonite gels (van Olphen, 1950) obtain a very reasonable explanation when the second picture is applied.

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