ANALYSIS OF CONSISTENCIES OF KAOLIN-WATER SYSTEMS BELOW THE PLASTIC RANGE[1]

By

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ABSTRACT

Consistency curves and characteristics of Newtonian, pseudoplastic, Bingham body, thixotropic and dilatant types of flow are reviewed. The theoretical effects of particle shape on effective hydrodynamic volume and shear resistance for ideal suspensions are considered.

The rheological properties of hydrogen and sodium mono base-exchanged kaolinite clays were determined, using a rotational viscometer, on slips containing up to 50 g solids per 100 g slurry. Changes in rheological properties were also evaluated as a hydrogen slip containing 20 g solids per 100 g slurry was converted into the sodium form.

The discussion includes the effect of differences in charges and charge distribution on the sodium and hydrogen particles and the resulting effects on particle orientation and flocculation. Correction factors for dissociation and particle interference have allowed the use of Einstein's equation for the viscosity of a suspension up to concentrations of about 40 percent solids for the hydrogen kaolinite system, and about 50 percent solids for the sodium kaolinite system.

INTRODUCTION

The forming of useful ceramic items from clay and water dates back to the early stages of our recorded history. Such applications have depended upon unique properties which are developed when clay is combined with water. In more recent history, in addition to the production of ceramic items, the role clay plays in our everyday life has been expanded further. The clay fraction affects the shear resistance of a silt or soil upon which a highway or bridge foundation might be built. The rheological properties of terrain over which a truck or tractor might be driven will be affected by the ratio of clay solids to water. And, as time goes on, technologists continue to expand the number of problems involving the properties of clay-water systems.

Rheology is defined as the study of flow and deformation of matter. Viscosity is the resistance experienced as one lamina layer flows over another lamina layer of the material. Yield value is the shearing force that will just cause flow between two adjacent layers of material.

In general, it is known that many factors affect the rheological properties of clay-water systems, but complete and precise data are not available. Among

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these factors are (1) the composition of the clay fraction, which might include one or more of the structures of kaolinite, montmorillonite, chlorite, mica, and interlayer mixtures; (2) the size and shape of the particles; (3) the nature and effect of the various associated adsorbed cations such as hydrogen, calcium, magnesium, and sodium; and (4) the clay to water ratio in the system.

In the past many workers have considered it satisfactory to describe the rheological properties of materials with a one point viscosity determination. Such evaluations are known as apparent viscosities and assume the material to be Newtonian, i.e., to have no yield value and to have a shearing stress that is directly proportional to the shear rate. For materials other than Newtonian this is not adequate. Fairly recent books (Green, 1949; Scott Blair, 1949) have more fully explained the reasons and advantages in using consistency curves in describing the rheological properties of materials. Consistency curves show how the yield point or viscosity, or both, of a material will vary under different flow conditions. When F is the force tending to slide one lamina layer past another and dv/dr is the change in flow rate of the material per unit distance between the lamina layers, then the viscosity, η, is defined by equation (1).

$$\eta = \frac{F}{dv/dr} \tag{1}$$

Frequently, rotating cup viscometers are used in obtaining consistency curves of materials. A plot of observed torque vs. revolutions per minute produces the consistency curve, which can be converted into actual viscosity and yield point data by use of instrument constants. Consistency curves have been classified into many types. Some of the major types are illustrated in Figure 1. Brief descriptions of the characteristics of materials or systems represented by these consistency curves are presented in the next few paragraphs.

Newtonian materials, illustrated in Figure 1-A, show a linear relationship between flow and shearing stress. These materials have loose, disconnected structures such as those found in gases, water, thin oils, and Einstein suspensions. There is neither structural breakdown nor orientation during flow.

Figure 1-B illustrates the consistency of pseudoplastic materials. Their flow increases faster than the shearing stress and the "down" curve is identical with the "up" curve. Resins, plastics, heavy oils, bitumens, and glass are pseudoplastics. In general these materials can best be studied at infinite dilution (when possible). Pseudoplastics have no thixotropic loop, and the change in flow characteristics is due to the long, curling, springlike molecules that are in a more ordered state when flowing (decreased entanglement).

Plastic or Bingham body type materials are represented in Figure 1-C. Jellies, soaps, plastics, fibers, metals, and some clay suspensions have a rate of flow that is proportional to shearing stress in excess of a yield value. Yield point and plastic viscosity values can be used to describe these systems. Yield point phenomena occur when energy is applied and consumed but produces no flow. In flocculated systems this could be due to the friction that particles exert upon themselves (internal pressure holding particles together). In both floc-
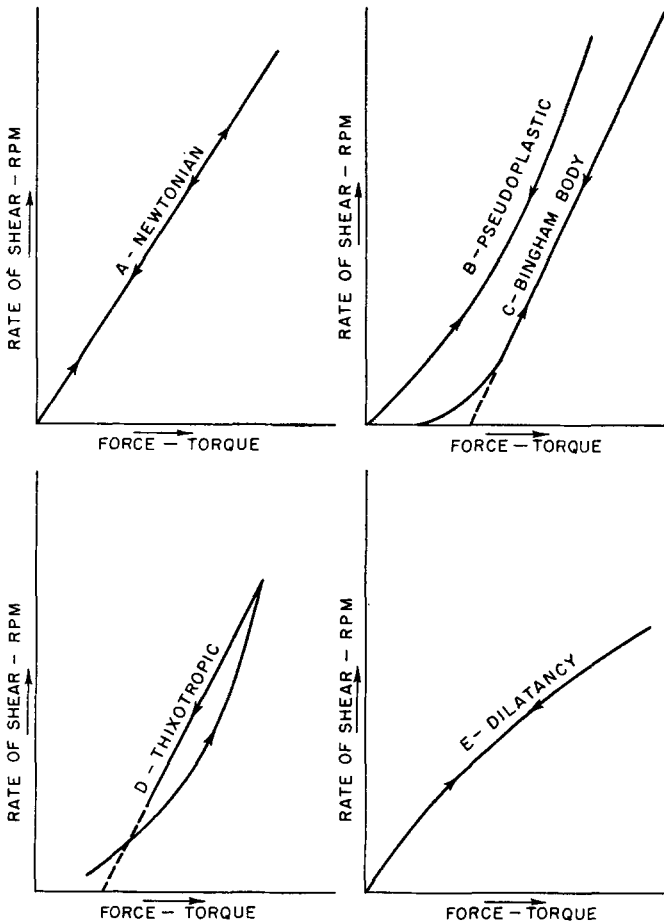
Figure 1. — Types of consistency curves.

culated and deflocculated systems this could be due to the alignment of charged particles, the resistance of contact, or the rotation of particles. Yield values are generally determined by extrapolation techniques. The actual values will vary somewhat and be dependent upon the manner in which the determinations are made.

Figure 1-D illustrates the consistency of thixotropic systems. In gels, sols, honey, clay-water dispersions, and other similar systems a hysteresis is observed between the consistency curves obtained when the rate of shear is being increased and when the rate of shear is being decreased. This hysteresis is due to isothermal processes such as particle alignment or breakdown of structures that re-form upon standing. The size of this loop is a function of time and de-

pends upon the degree of thixotropy present. Materials having thixotropic properties include those that develop loose, tangled structures, connected structures, and systems that align owing to repulsive charges on the particles. It is frequently necessary to describe these materials with a complete consistency curve, although yield point, plastic viscosity, and degree of thixotropy values will frequently describe them in a relatively satisfactory manner.

In dilatant flow the shearing stress increases faster than the rate of shear. Figure 1-E illustrates materials that are deflocculated particle suspensions in a settled state of minimum voids. An attempt to make such a system flow dilates the voids and thereby increases the resistance to flow. Such materials take on a dry appearance when pressure is applied to them. Sand in water and a paint pigment in oil are suspensions of this type.

Albert Einstein's (1906, 1911) mathematical study on fluid hydrodynamics considers the theoretical aspects and behavior of Newtonian disperse systems during shear. His study considers deviations from true theoretical behavior that are due to the presence of a disperse phase. The more important assumptions in this mathematical treatment are: (1) the particles are perfect spheres; (2) the spheres are rigid; (3) the particles are wet by the solvent; (4) the particles do not settle; and (5) no particle interference, which assumes no particle collisions and no electrical charge on the particles, exists. When η_0 is the viscosity of the solvent, θ is the volume fraction of the disperse phase, k is the shape factor (2.5 for spheres), then η, the viscosity of the suspension, is given by equation (2) which omits the higher order terms.

$$\eta = \eta_0(1 + k\theta) \qquad (2)$$

This equation simply states that the viscosity of an ideal suspension is a straight line function of the concentration and also is dependent upon the solvent viscosity and the shape of the particles (which should remain constant for any particular type of ideal system). It is interesting to note that Einstein's analysis is independent of particle-size distribution. This condition is valid as long as the other criteria of particle inertness and population are fulfilled.

Other workers (Jirgensons and Straumanis, 1954) have modified this equation and have defined some additional terms such as relative viscosity, η_{rel}, which is presented in equation (3).

$$\eta_{rel} = \eta/\eta_0 = 1 + k\theta \qquad (3)$$

Specific viscosity, η_{sp}, is presented in equation (4).

$$\eta_{sp} = \eta_{rel} - 1 = k\theta \qquad (4)$$

Einstein's mathematical treatment (1906, 1911) is for spheres. Other mathematicians have made similar reduced viscosity (defined later in equation 9) calculations for a number of common shapes, such as ellipsoids (Simha, 1940), lamellar discus (Peterlin and Stewart, 1938, 1939) and long rods (reviewed by Jirgensons and Straumanis, 1954). Respectively the reduced viscosity equations are (5), (6), (7), and (8).

$$[\eta] = 2.5 \qquad (5)$$

$$[\eta] = \frac{f}{15\,(\ln 2f - 3/2)} + \frac{f}{5\,(\ln 2f - 1/2)} + \frac{14}{15} \qquad (6)$$

$$[\eta] = 4/9 + 4/3\pi\,\frac{1}{d} \qquad (7)$$

$$[\eta] = 2.5 + \frac{f^2}{16} \qquad (8)$$

In the above equations $[\eta]$ is the reduced viscosity, f is the ratio length/average diameter and $1/d$ is the ratio of width/thickness of discus. Collectively they allow the rheologist to approximate viscosities that might be expected when ideal particles of known shape are the disperse phase in ideal suspensions. Figure 2 illustrates the effective hydrodynamic volumes that three different shapes (A, a sphere; B, a hexagonal disc; and C, a rectangular rod) would have when

A
SPHERE

B
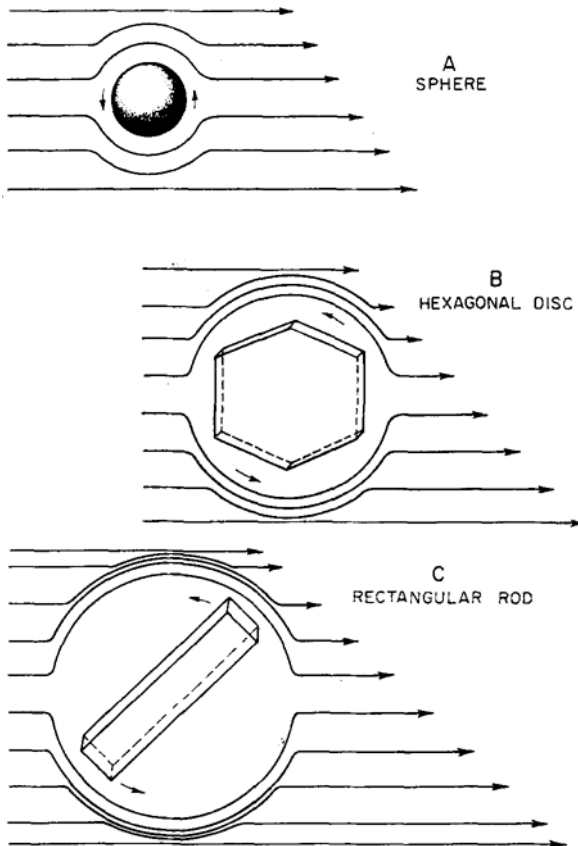HEXAGONAL DISC

C
RECTANGULAR ROD

FIGURE 2. — Hydrodynamic volumes.

suspended in a liquid under shearing conditions. The diagram has been drawn so that the solid volumes of these shapes are equivalent. As a point of interest it may be noted that, as the lamina layers move at different velocities, the layer moving at the highest velocity will tend to spin the particle in that direction. The tendency will be to orient the particles, and the particles that most nearly approach a sphere in shape will require the least energy. This is one factor in the development of a yield point or thixotropy, or both. After orientation one can also picture the change in plastic viscosity that will be due to the difference in energy required to force the fluid around and past the particles.

Nonideal conditions have sometimes made it desirable to evaluate empirically k, the shape factor, which is actually a constant compensation for the effective hydrodynamic volume of the particles. This is done by graphing η_{sp}/θ vs. θ, and taking the limit as $\theta \rightarrow 0$. This limit is known as the reduced viscosity, $[\eta]$, as indicated in equation (9)

$$[\eta] = \lim_{\theta \rightarrow 0} \frac{\eta_{sp}}{\theta} = k \tag{9}$$

In terms of flow classification characteristics previously described and illustrated in Figure 1, for very low clay to water ratios the system will exhibit Einsteinian characteristics and will be Newtonian. As the clay to water ratio is further increased particle interference during shear will cause departure from ideality, and the system might then be classed as pseudoplastic, Bingham body, or thixotropic. At still higher clay concentrations, insufficient solvent (water) may cause voids to develop during shear and the system would then be classified as dilatant.

The objectives of the present studies are: (1) to examine the rheological properties of kaolin clay-water systems over as wide a range as possible; (2) to present fundamental explanations for observed changes in viscosity and yield point phenomena; and, if possible, (3) to present a mathematical formula (possibly a modification of the Einstein equation) representing this information. At some time in the future attempts will be made to examine other types of clays and to obtain corresponding correlations.

EXPERIMENTAL

Testing Procedures

Clay concentrations in the suspensions tested are reported as grams of solids per 100 grams of slurry. This value was determined by drying 3- to 10-gram samples to constant weight at 105°C.

Specific gravity calculations were made by determining the ratio of slurry weight to water weight required to fill a graduate. A 50-ml graduated cylinder was used at room temperature for this purpose.

The pH of the clay suspensions was determined with a Beckman pH meter at room temperature. An electric motor-driven glass stirrer was used so as to obtain constant agitation during these determinations.

Total base-exchange capacity of the clay was determined by replacing the exchange ions with ammonium ions by the use of 1-N NH_4Ac solution. The excess ammonium acetate was removed by washing with 70 percent isopropyl alcohol in water solution. The amount of residual NH_4^+ adsorbed on the base-exchange sites of the clay was obtained by making a Kjeldahl distillation determination of nitrogen.

Base-exchange hydrogen was estimated by exchanging a clay slip sample in 0.5 N $BaCl_2$ solution and determining the amount of hydrogen liberated with standardized 0.1 N KOH caustic. Where Na^+ was present, the difference between the exchange capacity of the clay and the amount of hydrogen liberated in the $BaCl_2$ treatment was assumed to be base-exchange sodium. Excess sodium hydroxide was determined by titration using 0.1 N standardized sulfuric acid. All the above titrations were made to a pH of 7.0 using a Beckman pH meter.

A MacMichael rotating cup viscometer was used to obtain consistency curves. It consists of a bob which is suspended inside a rotating cup by means of a torsion wire. The material under test is placed in the annular space between the bob and the cup. When equilibrium is obtained while the cup is rotated at a constant rate, the force in equation (1) is measured by the torque in the suspension torsion wire, and the shear rate is proportional to the rate at which the cup is rotated. It is to be noted that the linear movement of the material being tested is zero at the bob surface and the same as the wall of the rotating cup at the outside edge of the annular space occupied by the material being tested. This condition assumes that there is no slippage between the material and either wall of the cup or the surface of the bob. The "up" consistency curves were obtained by taking uniform steps in increasing rotation rates at uniform time intervals. When the top speed of 48 rpm was reached, the "down" consistency curve was obtained immediately by decreasing the rpm in similar uniform steps. Manual control of the steps produced some variation in their size. However, when this variation was thought to be too great, the whole measurement procedure was repeated. The twist or deflection in the calibrated wire was measured at the end of each time interval. The consistency curves of rpm vs. twist in the calibrated wire were plotted. Plastic viscosity and yield point values were then calculated using instrument constants that were determined with standard viscosity oils obtained from the U. S. Bureau of Standards.

The viscometer used in this work developed a maximum shear rate of 30 sec^{-1}. Published consistency curves (Moore and Davies, 1956) of ceramic slips containing about 10 percent solids indicate that shear rates in excess of 200 sec^{-1} were necessary to produce the straight line portion of the curve. Calculations using the indicated viscosity and yield point (Green, 1949) indicate that a minimum shear rate of about 375 sec^{-1} would be necessary to produce laminar flow. Nevertheless, consistency curves approach this straight line viscosity relationship asymptotically and observations taken at lower shear rates may vary only slightly from true values. The data obtained in this work are assumed to represent comparable relative rheological values, and they have

TABLE 1. — PROPERTIES OF HYDROGEN-KAOLINITE SUSPENSIONS

Sample Number	Slurry Conc.[1]	pH	Specific Gravity	Yield Point dynes/cm^2	Plastic Viscosity at Different Shear Rates (poise)				
					15 rpm	25 rpm	35 rpm	42 rpm	48 rpm
DRG-5-1	0.36	5.65	1.002	....	0.0068	0.0078	0.0097	0.0116	0.0116
DRG-5-2	0.62	5.68	1.005	....	0.0097	0.0097	0.0116	0.0118	0.0114
DRG-5-3	1.2	5.37	1.011	....	0.0078	0.0107	0.0126	0.0145	0.0145
DRG-5-4	4.4	4.88	1.022	....	0.0257	0.0257	0.0257	0.0257	0.0257
DRG-5-5	8.0	4.60	1.048	10.7	0.0388	0.0316	0.0316	0.0316	0.0316
DRG-5-6	14.1	2	1.097	221	0.258	0.351	0.433	0.457	0.469
DRG-5-7	25.2	2	1.180	1,575	....	0.99	1.23	1.70	1.82
DRG-5-8	36.5	2	1.267	7,200	15.5	11.3	7.05	5.64	5.64
DRG-5-9[3]	62.9	2	1.732						

[1] Grams solids per 100 grams slurry.
[2] Sample discarded before value obtained.
[3] Too thick for operation of MacMichael viscometer.

been used in analyzing and considering the mechanism involved in the shearing of kaolinite-water suspensions. It must be emphasized that for these slips, in the cases when laminar flow was not obtained as discussed above, the indicated plastic viscosity values are higher and the indicated yield point values are lower than the true values.

Preparation and Testing of Samples

Hydrogen kaolinite.—A stock of hydrogen kaolinite was prepared from commercial DRG clay.[1] The clay was first washed with a dilute hydrochloric acid solution and then with distilled water until free of excess chloride ions. As an example of this laboratory procedure, batch no. 5 was prepared by working with one kilogram of clay in a five gallon pyrex solution bottle. Ten acid washings, each consisting of 20 ml of concentrated hydrochloric acid in 4 gallons of distilled water, were followed by fourteen 4-gallon distilled water washes. The clear supernatant liquor was separated from the solids by decantation after each acidification or wash step. The pH of the distilled water used was 5.65, and the pH of the final decanted liquor from the slurry was 5.3 when chlorine ions were no longer detected with $N/10$ silver nitrate solution.

From this base stock of hydrogen kaolinite slurry, a series of suspensions were prepared with different concentrations of clay solids. In some cases water was extracted by filtration and in others distilled water was used to dilute the suspension. Table 1 summarizes data on hydrogen kaolinite suspensions which include samples numbered DRG-5-1 to DRG-5-9. Concentration, pH, specific gravity, and consistency evaluations were made on these samples. It is to be noted that the consistency data are summarized by tabulating the plastic vis-

[1] X-ray and D.T.A. studies showed that this Georgia kaolin did not have any detectable accessory minerals associated with the well-crystallized kaolinite.

TABLE 2. — PROPERTIES OF SODIUM-KAOLINITE SUSPENSIONS

Sample Number	Slurry Conc.[1]	pH	N_{Na+}[2]	Specific Gravity	Yield Point dynes/cm²	Plastic Viscosity at Different Shear Rates				
						15 rpm	25 rpm	35 rpm	42 rpm	48 rpm
DRG-5-11	0.73	7.36	....	1.004	....	0.0058	0.0093	0.0103	0.0116	0.0120
DRG-5-12	1.13	7.45	....	1.007	....	0.0058	0.0068	0.0101	0.0116	0.0122
DRG-5-13	2.26	7.85	....	1.013	....	0.0077	0.0097	0.0116	0.0122	0.0126
DRG-5-14	5.22	8.20	....	1.036	....	0.0087	0.0101	0.0116	0.0126	0.0126
DRG-5-15	9.00	8.19	0.91	1.055	....	0.0087	0.0103	0.0122	0.0136	0.0147
DRG-5-16	27.6	7.65	0.90	1.214	4	0.0485	0.0485	0.0485	0.0485	0.0485
DRG-5-17	37.9	7.58	0.91	1.313	207	0.307	0.271	0.257	0.242	0.204
DRG-5-18	48.7	7.52	....	1.436	2,100	2.52	1.76	1.52	1.52	1.40
DRG-5-19[3]	61.9	7.00	....	....						

[1] Grams solids per 100 grams slurry.
[2] Mole fraction sodium on the base exchange sites was not determined on all of the samples in this series.
[3] Too thick for determination on MacMichael viscometer.

cosity at a number of different shear rates and the indicated yield point. If desired, consistency curves may be reconstructed from these data.

Sodium kaolinite.—After inspection of the hydrogen kaolinite suspensions, the clay was collected and a portion of it converted into the sodium form by titration to 7.2 pH with sodium hydroxide solution.[1] This sodium kaolinite stock suspension was then used to prepare a series of suspensions having various concentrations of solids. Sodium kaolinite suspensions include samples DRG-5-11 to DRG-5-19. Evaluations similar to those performed on the hydrogen kaolinite were made and are summarized in Table 2. The observed relationships between clay concentration vs. plastic viscosity and yield point for both hydrogen and sodium kaolinite are shown graphically in Figures 3 and 4.

Titration and testing of hydrogen-sodium kaolinite series.—A hydrogen kaolinite suspension was alkalized by the addition of small increments of sodium hydroxide. About one liter of slurry, which contained 19.6 g solids per 100 g slurry was treated with small increments of normal sodium hydroxide solution. After each caustic addition the suspension was agitated and allowed to stand 24 hours to reach equilibrium. Small amounts of slurry were then withdrawn and analytical and consistency evaluations were made as summarized in Table 3. A pH greater than 9 was required before no base-exchange hydrogen was found when the clay was treated with BaCl₂ solution; i.e., all the base-exchange sites can be considered occupied by sodium when the pH is greater than 9. Figures 5, 6, and 7 show graphically how the hydrogen kaolinite suspension properties change as the suspension is titrated with sodium hydroxide. The abscissa index is on the basis of meq of sodium added per meq of base-exchange capacity of the clay. It is interesting to note that the rapid change in pH occurs when the amount of sodium added to the slurry is equival-

[1] Later analytical work indicated that this material had base-exchange ions that were 90 percent sodium and 10 percent hydrogen.

ent to the exchange capacity of the clay in the suspension. Each withdrawn sample was discarded after its properties were determined, making the final volume about 0.35 liters less than at the start.

In the above neutralization reaction no residual anions or cations are present after completion of each reaction. The sodium replaces hydrogen which combines with hydroxyl to form water, which was already present in excess.

RESULTS AND DISCUSSION

Effective Particle Volume

In systems containing a disperse phase, such as clay in water, two types of electrical charge can be considered. First, the solid disperse phase may be charged. These charges may be due to isomorphous substitution in the clay lattice, to broken edge bonds, or simply to adsorbed ions. Clay solids are usually negatively charged and act as anions.

The other type of charge is due to the counter cations that are in the liquid phase of the dispersing medium. These cations are grouped around the negatively charged solid clay particles. Thus, in the region of the charged particle,
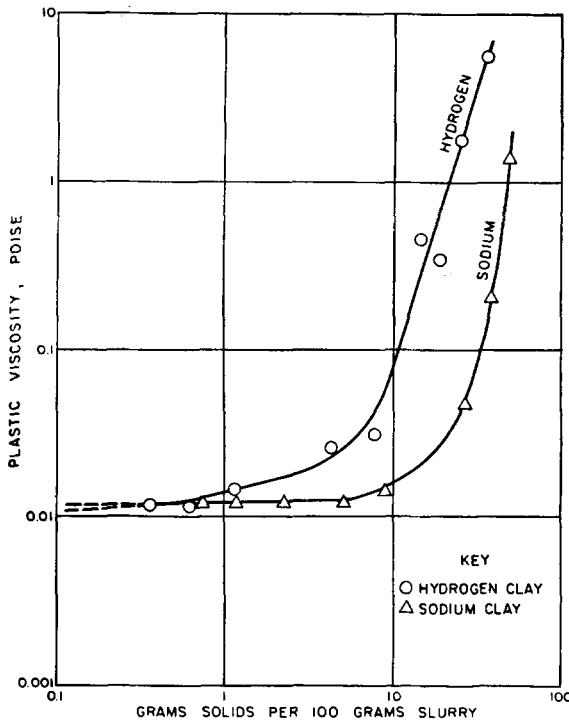

FIGURE 3. — Plastic viscosity vs. clay concentration for hydrogen- and sodium-kaolinite.
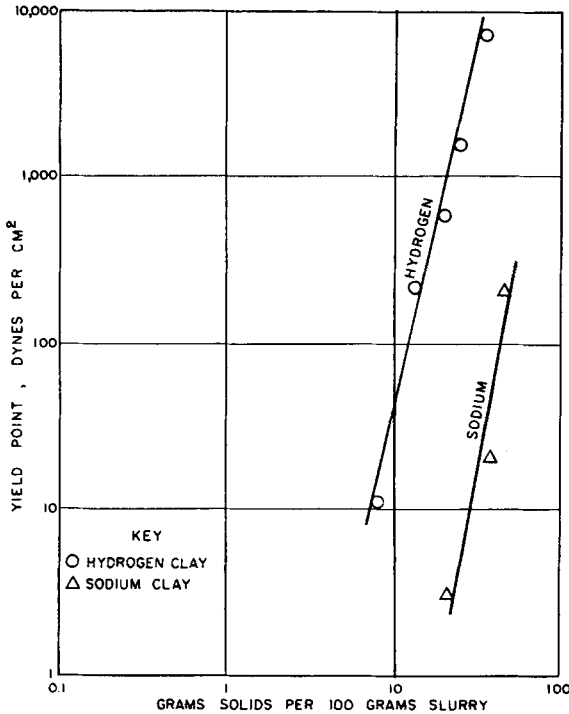
FIGURE 4. — Yield point vs. clay concentration for hydrogen- and sodium-kaolinite.

one finds a diffuse double layer that tends to produce a neutralized particle, but the outer shells of counter cations of similar particles will be of a similar charge and the tendency will be for them to repel each other, thus producing a dispersion. This double layer of ions can be compared to a condenser; thus, a potential gradient exists through the layer. The Helmholtz statement of this principle pictures the actual charge on a particle as balanced by another layer of oppositely charged ions immediately adjacent to it. The Gouy-Stern modification pictures this outer layer of ions as a diffuse cloud, with individual ions being more or less free to move, yet still under the influence of the particle. Such movement of these cations from the solid particle, or expansion of the hydrodynamic volume, is termed dissociation in this paper. Thus, effective hydrodynamic volume will vary with the degree of dissociation. The thickness and rigidity of this ionic cloud will depend upon the nature and concentration of the particles, ions, and ion concentration composing the counter layer, as well as the solvent. In considering the hydrodynamic properties of a dispersed phase particle, the fixed outer layer which contains the counter ions is considered part of the actual particle.

   Clay-water suspensions are thus not ideal in the Einstein sense, and at lower clay to water ratios the relative number of cations dissociating from the actual

TABLE 3. — CONVERSION OF HYDROGEN- TO SODIUM-KAOLINITE

Sample	pH	N_H^+ $(1-N_{Na^+})^1$	Excess Na$^+$ meq/meq clay^1	meq Na$^+$ added per meq clay^2	Yield Pt. dynes per cm^2	Plastic Viscosity (Poise)				
						15 rpm	From Slope of Down Curve			
							25 rpm	35 rpm	42 rpm	48 rpm
DRG-5a	4.45	1.000	....	....	653	0.99	0.88	0.70	0.36	0.36
DRG-5b	5.98	0.855	....	0.26	476	0.64	0.58	0.41	0.35	0.35
DRG-5c	6.33	0.644	....	0.32	373	0.53	0.35	0.18	0.18	0.18
DRG-5d	6.59	0.400	....	0.47	337	0.41	0.35	0.29	0.23	0.23
DRG-5e	6.81	0.367	....	0.64	302	0.41	0.35	0.18	0.18	0.18
DRG-5f	7.21	0.185	....	0.79	167	0.41	0.18	0.14	0.14	0.14
DRG-5g	9.14	0.041	....	0.95	....	0.0087	0.0097	0.0155	0.027	0.029
DRG-5h	10.12	....	0.09	1.05	....	0.0078	0.0107	0.0145	0.0145	0.0165
DRG-5i	10.62	....	0.20	1.27	....	0.0087	0.0107	0.0136	0.0184	0.0184
DRG-5j	10.96	....	0.33	1.43	....	0.0087	0.0116	0.0155	0.0136	0.0155
DRG-5k	11.29	....	0.48	1.75	....	0.0087	0.0107	0.0126	0.0155	0.0165
DRG-5l	11.52	....	1.04	2.06	....	0.0084	0.0128	0.0136	0.0144	0.0144
DRG-5m	11.67	....	1.39	2.38	....	0.0088	0.0120	0.0168	0.0168	0.0168
DRG-5n	11.77	....	1.60	2.70	....	0.0088	0.0136	0.0144	0.0152	0.0152
DRG-5o	11.93	....	2.35	3.17	....	0.0088	0.0120	0.0144	0.0176	0.0176
DRG-5p	12.06	....	4.45	5.44	....	0.0096	0.0128	0.0152	0.0184	0.0208

[1] By analysis of the liquor suspending the clay after exchanging in neutral BaCl$_2$ solution (0.5 N).
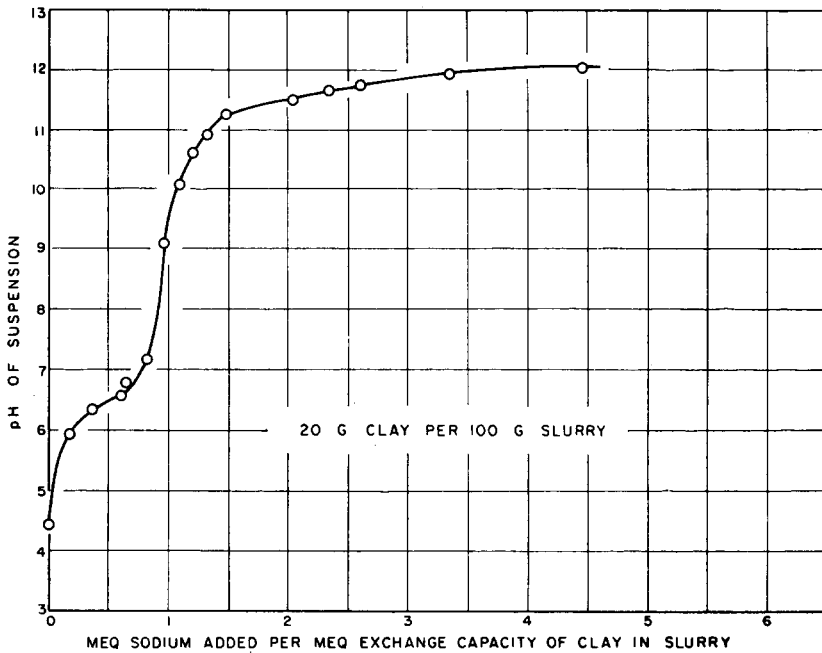
[2] NaOH added to suspension.

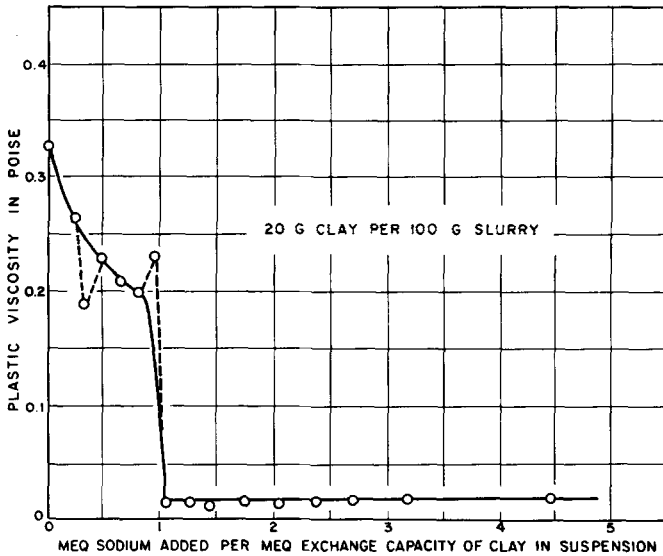FIGURE 5. — pH of suspension as hydrogen-kaolinite is titrated with sodium hydroxide.

FIGURE 6. — Sodium hydroxide titration of hydrogen-kaolinite: the effect on plastic viscosity.

clay surface into the Gouy-Stern layer increases. This dissociation causes the relative effective volume to increase and also causes the shape factor to approach that for a sphere. If γ is used as a correction factor, the product $\gamma\theta_{solid}$, will represent the effective hydrodynamic volume, and equation (10) will be a modification of the Einstein equation when θ_{solid} is the actual weight fraction of the solid. γ will correct for non-ideality of the suspension and will also include such factors as dissociation and density of the effective particle, as well as repulsion effects due to the electrostatic charges on the particles or particle collisions, or both. Variations in particle-size distribution will also be reflected in this correction factor by their effect on the over-all hydrodynamic volume.

$$\eta_{sp} = k\gamma\theta_{solid} \tag{10}$$

Table 4, Viscosity Correction Factors, and Figure 8, Calculation of Viscosity Correction Factors, present data showing the relationship between η_{sp}/θ_{solid} or $k\gamma$ vs. θ_{solid} for the hydrogen and sodium kaolinite-water systems (up to 40 and 50 percent solids by weight respectively). Figure 8 indicates that the relationship between concentration and $k\gamma$ follows two definite laws.

Consideration of the data at lower concentrations indicates that dissociation has probably increased the effective hydrodynamic volume to the extent that the radius of particles at zero concentration when studied in a rectangular coordinate plot would be approximately three times the radius of the particles when particle interference is first observed. Figure 8 also indicates that the hydrodynamic volume for the Na-clay particle is greater than for the H-clay particle. This observation is in agreement with that pictured in the literature (Johnson and Norton, 1941). Exact figures cannot be presented as exact shapes
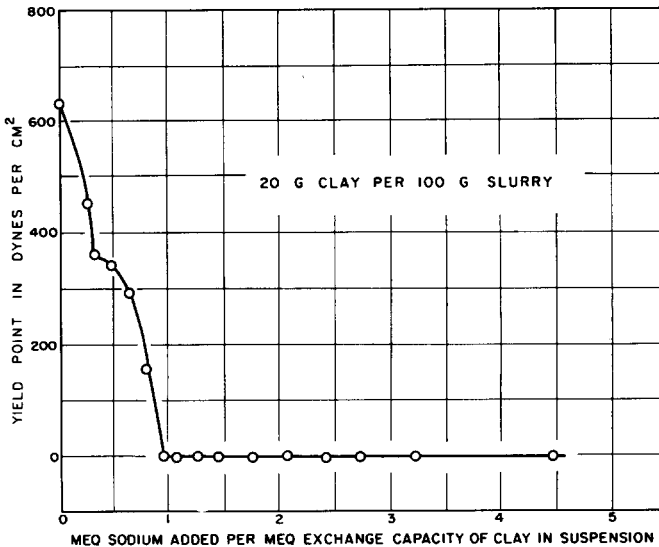
FIGURE 7. — Sodium hydroxide titration of hydrogen-kaolinite: the effect on yield point.

and volumes are not known. As the clay concentration increases, the volume containing the required counter ions decreases rapidly owing to the decreased degree of dissociation and to the crowding due to the increased number of particles. During this period further departure from Einstein's law occurs because of orientation of particles or deformation of the diffuse double layer, or both.

At still higher concentrations actual particle collisions and favorable packing distributions contribute to shear resistance and measurable yield points develop. From Figure 8 it is noted that the $k\gamma$ component can now be written $k(\gamma_h + \gamma_c)$ when γ_h and γ_c are respectively the effects due to dissociation and to crowding and collisions, as discussed above. The modified Einstein equation can now be written as in equation (11).

$$\eta = \eta_0[1 + k(\gamma_h + \gamma_c)\theta_{solid}] \qquad (11)$$

These modifications for the Einstein equation can be primarily considered corrections for effective hydrodynamic volume at lower concentrations and also for particle interference at higher concentrations. Systems having a preferred orientation, or flocculation of particles, that are disturbed under shear and that resume their original distribution after standing will exhibit thixotropic characteristics. The above picture is obtained in considering either the hydrogen-kaolinite-water or the sodium-kaolinite-water systems.

Comparison of Hydrogen and Sodium Kaolinite Forms

In comparing the rheological data for the hydrogen- and sodium-kaolinite-water systems, Figures 3 and 8 disclose no difference in viscosity at a concen-

TABLE 4. — VISCOSITY CORRECTION FACTORS

θsolids Gram Solids per Gram Slurry	Viscosity Poise	η_{rel}[1]	η_{sp}	$\dfrac{\eta_{sp}}{\theta_{solid}}$
Hydrogen-Kaolinite Suspensions				
0.005	0.0122	1.37	0.37	74
0.01	0.014	1.57	0.57	57
0.015	0.0155	1.74	0.74	49
0.02	0.017	1.91	0.91	45.4
0.05	0.025	2.82	1.82	36.4
0.10	0.10	11.22	10.22	102
0.20	0.85	95.5	94.5	472
0.30	3.6	405	404	1,345
0.40	8.0	900	899	2,250
Sodium-Kaolinite Suspensions				
0.005	0.012	1.35	0.35	70
0.01	0.0123	1.38	0.38	38
0.015	0.0125	1.40	0.40	27
0.02	0.0128	1.44	0.44	22
0.05	0.0130	1.46	0.46	9.2
0.10	0.0154	1.73	0.73	7.3
0.20	0.27	30.3	29.3	146
0.30	0.77	77.7	77	256
0.40	3.0	303	302	755
0.50	11.8	1,330	1,329	2,660

[1] Relative viscosity of water, 0.0089 poise at 25°C.

tration of about 0.7 g solids per 100 g slurry. Below this concentration the hydrogen form has a lower viscosity, and above, a higher viscosity. Kaolinite is described (Schofield and Sampson, 1953) as having basal surfaces with negative charges and edges that may be positive, negative, or uncharged depending upon the pH of the solvent. In general, it is assumed that the edge charges of kaolinite particles are positive at low pH and negative at higher pH values. The position that cations would take in the dissociated form would influence the shape of the diffuse double layer. Thus, it would be expected that the hydrogen particles would be more nearly spherical than the sodium particles. Therefore, the phenomena of higher viscosities for very low-concentration sodium suspensions could be due to a larger shape factor, k, in the Einstein equation or a large hydrodynamic volume, γ_h, due to dissociation, or both.

Table 3 and Figures 5, 6, and 7 present data showing changes in rheological properties as a hydrogen clay slurry containing about 20 g of solids per 100 g slurry was converted into the sodium form. Conversion into the deflocculated sodium form involves a sharp and large reduction in plastic viscosity as well as the disappearance of the yield point at a pH of about 7 to 9 for this clay concentration. Visual observations of suspensions based primarily on settled bulk clay volumes for the more concentrated suspensions suggest that the ef-
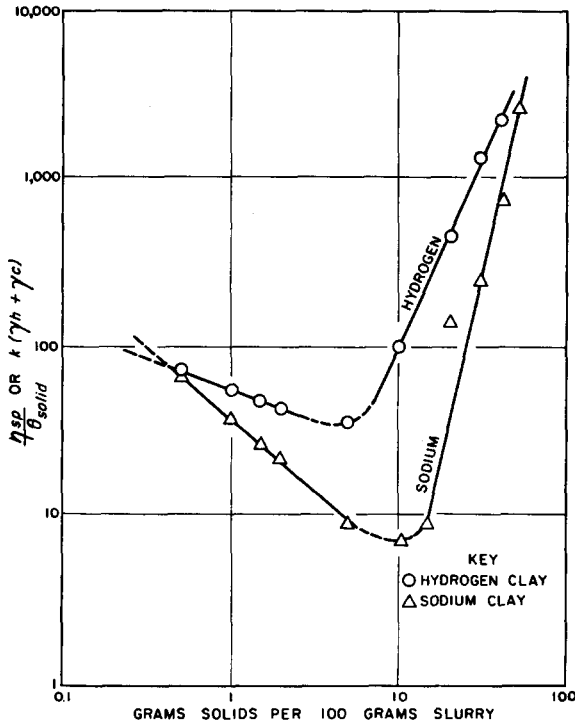
FIGURE 8. — Calculation of viscosity correction factors.

fective sodium-kaolinite particles or aggregates are smaller than the effective
hydrogen-kaolinite particles which appear to be large, flaky, and voluminous.

In general several explanations were thought possible to account for the in-
creased shear resistance found in the hydrogen slurry. Possible factors include
changes in the shape factor or the hydrodynamic volume factor, or a combi-
nation of these.

If one considers the data in Table 3 and assumes that the difference is due
only to changes in the shape factor, calculations indicate that the shape factor
of the hydrogen-kaolinite would have to be 48 times larger than that of the so-
dium-kaolinite. Assuming a $6\frac{1}{2}$ to 1, l to d ratio, for sodium-kaolinite disclike
particles, a 310 to 1, l to d ratio, would be needed in the hydrogen-kaolinite part-
icles to account for this change in plastic viscosity. This possibility is rejected
as being illogical.

In a similar manner, if only the hydrodynamic volume of the particles is con-
sidered, it would be necessary for the individual hydrogen-clay particles to have
an effective volume 48 times that of the sodium particles (equivalent to 3.6
times the radius). Owing to the actual volumes of the solid and water under
consideration, this possibility is rejected because of an insufficient amount of

water. Also, the relative degree of dissociation of the two types of clays would not be expected to be reversed at higher concentrations.

Finally, a change involving both the shape and volume factors can be pictured based on flocculation or formation of aggregates. As previously mentioned, Schofield and Sampson (1953) described kaolinite as having negative charges on the basal surfaces and edge charges that are sensitive to pH. At low pH values these edge charges are positive, and at high pH values they are negative. Thus, in this work sodium-clay particles are pictured as being essentially individual clay particles surrounded by a diffuse layer of sodium cations. The hydrogen-clay particles, on the other hand, are pictured as having the edges associated with hydroxyl ions and the basal faces with hydrogen ions. On this basis, flocculation of hydrogen particles would be expected. It is possible that the formation of hydrogen-kaolinite aggregates is a function of concentration as well as pH. As edge-to-face bondings occur to form agglomerates, large amounts of water will be occluded in a honeycomblike structure, thus reducing the amount of water available as a solvent and correspondingly increasing γ. At the lower concentrations, even though flocculation may be occurring, the number of particles or aggregates may not be sufficient to cause particle interference or shear resistance. The concentration at which this effect begins corresponds to the point at which measurable yield points begin to develop and the γ_c factor, mentioned previously, becomes dominant. Figure 8 shows this effect by the straight-line relationship of opposite slope at higher clay concentrations.

The sodium-clay, even though it probably does not have extensive flocculation, also develops a yield point and has a rapid increase in viscosity at some concentration owing to particle interference and some preferred orientation that may occur owing to some differences in charge distribution. This concentration is higher than that for the corresponding point in the hydrogen-clay system because water is not immobilized by edge-to-face flocculation.

In order to check this analysis it would be interesting to prepare a series of kaolinite slurries having a given concentration with a progressive change from hydrogen to a sodium form, to freeze these structures, and then to examine them using such instruments as the electron microscope, optical microscope, and x-ray diffractometer.

CONCLUSIONS

(1) Individual kaolinite-suspension particles are pictured as solid particles surrounded by a diffuse double layer of counter ions that is referred to as the Gouy-Stern layer. Variations in the effective hydrodynamic volume are affected by the number and degree of dissociation of ions that are free of the solid particle but are still within this layer. Increased particle concentration reduces the effective volume because the degree of dissociation is reduced. Kaolinite particles are presented as having negative charges on their basal surfaces and charges on the edges that are sensitive to pH. At high pH values these edge charges are negative, and at low pH values they are positive. Under these

conditions agglomeration or flocculation of hydrogen-kaolinite particles, due to positive edges, may occur by a mechanism described as face-to-edge bonding. Face-to-edge bonding reduces the amount of water available as a solvent because of its immobilization in the resultant honeycomb structure. Natural distribution of differences in charge density on sodium-kaolinite particles, due to negative edges, can also produce a preferred orientation although actual flocculation may not occur. When an oriented or flocculated system that is disturbed by shearing returns to its original condition upon standing, the system is said to exhibit thixotropic characteristics. Brownian movement and force fields can aid in the re-forming of a preferred orientation or some equilibrium edge-to-face bonding.

(2) At very low clay to water ratios the lower viscosity of hydrogen-kaolinite-water systems, as compared to sodium-kaolinite-water systems, is thought to be due largely to the hydrogen disclike particles having negatively charged faces and positively charged edges which produce a more nearly spherical hydrodynamic particle than the sodium form, which is described as negatively charged on both the face and edge. Another possible factor is that the Na-clay particle dissociates to a greater degree.

(3) In the hydrogen-kaolinite-water system, at higher concentrations, a greater degree of face-to-edge bonding produces more flocculation. These flocks contain large amounts of occluded water, which effectively reduces the amount of water available as a solvent, thus increasing the shear resistance and particle interference owing to the crowding of the system and producing a yield point. In the sodium-kaolinite-water system at higher concentrations there is less, or no, face-to-edge bonding and the sodium particles are relatively deflocculated; this accounts for the higher fluidity and lower yield points of these systems relative to the hydrogen systems at equivalent concentration.

(4) Thus, clay suspensions are not ideal; however, Einstein's equation for the viscosity of a suspension can be used when correction factors for effective hydrodynamic volume or particle interference, or both, are used in addition to the shape factor. The effective hydrodynamic volume depends on the degree of dissociation, electrostatic repulsion, and flocculation. The over-all effect of factors can be obtained from a plot such as is shown in Figure 8. This particular plot indicates that all these particle interference factors become the controlling factor above about 5 percent solids for the hydrogen-kaolinite-water system, and about 11 percent solids for the sodium-kaolinite-water system for the DRG clay studied. The modified Einstein equation thus proposed is

$$\eta = \eta_0 \left[1 + k(\gamma_h + \gamma_c) \theta_{solid} \right] \tag{11}$$

in which γ_h and γ_c are definitely functions of the concentration and particle-size distribution.

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