

LATTICE EXPANSION AND RHEOLOGICAL BEHAVIOR RELATIONSHIPS IN WATER-MONTMORILLONITE SYSTEMS

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ABSTRACT

Some divergent experimental data have been reported on the swelling behavior of sodium montmorillonite. At water contents above 50 percent (based on the weight of dry clay) the basal reflection of sodium montmorillonite at 19.2 Å becomes weak and very diffuse; some workers have stated that it disappears altogether while others report a persistent weak line even at very high water content. The pronounced differences in physical properties of sodium and calcium montmorillonite suggest that their lattice expansions should also be dissimilar. This paper describes some X-ray diffraction experiments using purified lithium, sodium, and potassium montmorillonites dispersed in water and in salt solutions which were conducted for the purpose of resolving some of these disputed points. The X-ray diffraction instrument employed was a General Electric geiger counter spectrometer unit with a copper tube and nickel filters. The knowledge thus gained has provided some insight into other properties of these clays, such as their rheological behavior.

A recording Couette-type viscometer designed to provide a wide spectrum of shear rates and shearing stresses has been used to examine the rheological transformations which occur in passing from states of maximum dispersion to states of varying degrees of agglomeration as a result of interactions between LiCl, NaCl, KCl, and CaCl₂, and the Li, Na, K, and Ca salts of montmorillonite in terms of certain ideal rheological models. Filtration characteristics of these systems have also been explored using a standard technique.

PART I — X-RAY DIFFRACTION STUDIES *

INTRODUCTION

The first paper on the lattice expansion of montmorillonite in water, by Hofmann, Endell, and Wilm (1933, p. 340) appeared in 1933. Since then, this mineral has been the subject of many investigations of this kind. General agreement exists on the expansion properties of montmorillonite saturated with Ca⁺⁺ and H⁺ ions. These expand in excess water to 19 Å and 22 Å respectively. However, divergent experimental data have been reported on the swelling behavior of the sodium derivative. At water to clay ratios

* The authors wish to acknowledge a paper which appeared in the February 6, 1954 edition of *Nature*, by K. Norrish and J. P. Quirk, entitled "Crystalline Swelling of Montmorillonite." Described therein are X-ray diffraction experiments on sodium montmorillonite similar to those discussed in this paper. The two sets of data are in substantial agreement.

above 0.5 (based on the weight of dry clay) the first basal reflection of sodium montmorillonite at about 19 Å becomes weak and diffuse. Mering (1946, p. 205) has stated that it disappears altogether and that crystalline expansion ceases above 20 Å. Hofmann and Bilke (1936, p. 239) reported a reflection in excess of 30 Å. Recently Collis-George and Bodman (1954) reported a persistent 19.2 Å line for sodium montmorillonite at very high water content. The dissimilarities in physical properties of calcium montmorillonite-water and sodium montmorillonite-water systems suggest that the lattice expansion properties of these clays should also be dissimilar.

This paper describes some X-ray diffraction experiments using purified lithium, sodium, and potassium montmorillonites dispersed in water and in salt solutions which were conducted in the hope that some of the disputed points concerning the lattice expansion of monovalent montmorillonites could be resolved. The results have provided some insight into other properties of these clays, such as their rheological behavior.

EXPERIMENTAL PROCEDURES

Preparation of Purified Clays

The bentonite used in this work was of the Belle Fourche variety.† The following procedure was adopted for the preparation of the pure clays. A one weight percent suspension of the raw clay was kept at 76.6° C for twenty-four hours. After another twenty-four hours at room temperature, those solids which had settled from the suspension were removed and sufficient HCl was added to make the slurry 0.1N. The resulting hydrogen clay was washed with distilled water until the specific conductivity of the filtrate from a one weight percent suspension was below 10^{-6} mhos. Four batches prepared in this way were neutralized with lithium, sodium, potassium, and calcium hydroxides. Equivalence points were determined by the conductometric titration method. The only impurity found by subsequent X-ray diffraction analysis was quartz, present in about two percent by weight. Rheological measurements using these four clays are described in Part II and were carried out on samples with quartz present. For the X-ray diffraction work, quartz-free lithium, sodium and potassium montmorillonites of less than one-tenth micron settling radius was obtained by centrifugation in a Sharples super-centrifuge.

Preparation of Specimens for X-Ray Diffraction

Two types of diffraction samples were devised for the clay-water systems. Thin flat films, prepared after the manner of Bradley, Grim, and Clark (1937, p. 216) were equilibrated over sulfuric acid solutions at relative humidities from 0.0 percent to 99.5 percent. Using these, systems with water to clay ratios from 0.0 to about 0.5 could be examined. For higher

† Purchased in 1947 from the Hancock Mud Sales and Service Company, Houston, Texas.

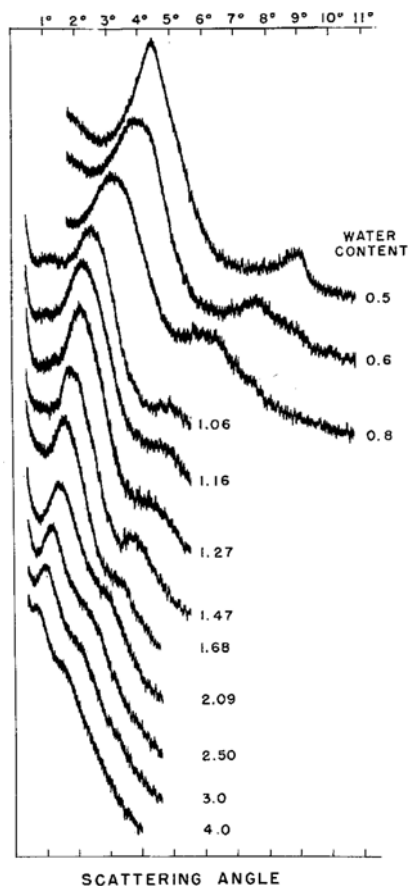


FIGURE 1.—Diffraction pattern of (001) and (002) from lithium montmorillonite containing various amounts of water.

water contents, clay, dried at 75°C and ground to pass a 200 mesh screen, was added to varying amounts of water, sealed in polyethylene bags, and milled till homogeneous. Equilibration time for the films was one month, for the gels, one week. With this combination, water to clay ratios from 0.0 to 5.0 were handled.

In similar fashion, clay-water-electrolyte systems were prepared in sealed polyethylene bags. No differences were noted as the order of addition of the components was changed.

Throughout, reflection patterns were obtained on a General Electric XRD-3 unit (Geiger Counter Spectrometer attached) with copper target and nickel filters. A metal housing containing thin-aluminum windows covered the samples during exposure. For the films, the correct relative humidity was maintained within the housing with acid solutions; for the

gels, pure water was used and the diffraction patterns were obtained as rapidly as possible. A gearing modification in the chart recorder was made which permitted a slow scan of 0.2° per minute and a chart speed of 0.2 inches per minute. Typical diffraction patterns obtained with this technique are shown for lithium montmorillonite in Figure 1.

DISCUSSION OF RESULTS

Montmorillonite-Water Systems

In Figures 2, 3, and 4 the observed (001) spacings of lithium, sodium, and potassium montmorillonites are shown for a large range of water to clay ratios. As has been previously reported, the initial water is adsorbed in 3 Å layers. As the first two layers are fixed, the (001) spacings do not increase at constant rates with water adsorption. Assuming that all adsorbed water occupies positions between the sheets, the gross density of the interlamellar water varies in periodic fashion reaching maximum values as the first and second layers are completed. However, as the third layers are fixed in lithium and sodium montmorillonites, no unfilled volume is created. This is not unexpected since the relative humidity is above 90 percent in both cases.

The lithium clay continues to expand in a continuous regular manner as water is added. At a water to clay ratio of 4.0, a (001) spacing of 117 Å is reached. At a ratio of 5.0 the line is so weak that an angle measurement is not possible and at 6.0 it has disappeared.

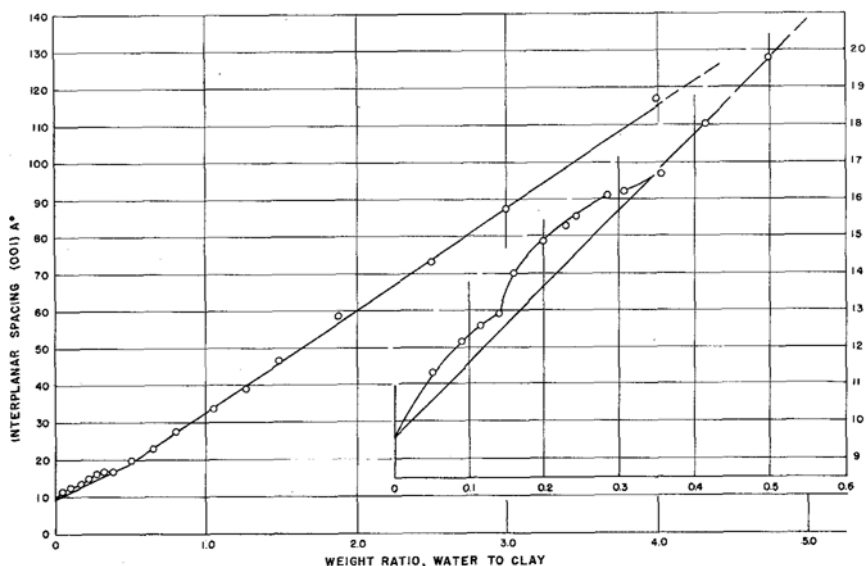


FIGURE 2.— Lattice expansion of lithium montmorillonite.

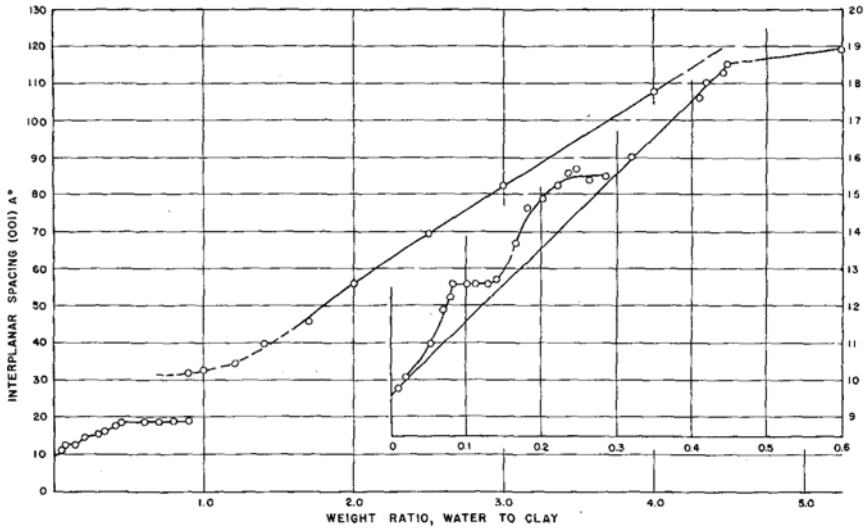


FIGURE 3.— Lattice expansion of sodium montmorillonite.

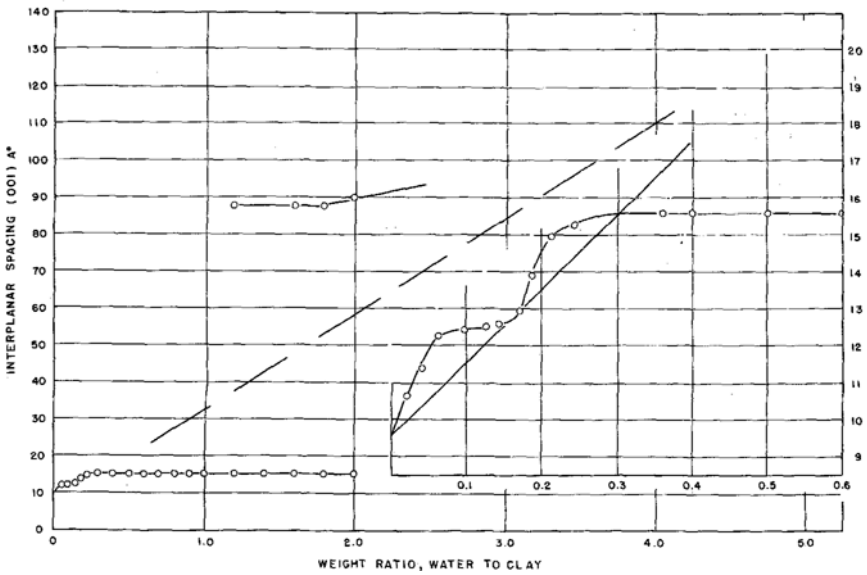


FIGURE 4.— Lattice expansion of potassium montmorillonite.

Between water to clay ratios of 0.5 and 1.2, a discontinuous increase in spacing occurs in sodium montmorillonite and no lines between 19.2 Å and 31 Å are observed. In this region the addition of water increases the intensity of the 31 Å line and correspondingly decreases that of the 19.2 Å line. When the latter has vanished, expansion again proceeds continuously as water is added. A spacing of 108 Å is reached at a water to clay ratio of 4.0.

A much more pronounced discontinuity begins at 15.6 Å in the potassium clay. A weak and diffuse line appears at 88 Å between ratios of 1.2 and 2.0, a range in which the 15.6 Å steadily decreases.

Montmorillonite-Water-Electrolyte Systems

The lattice expansion process can be retarded through the addition of electrolytes. The effects of lithium, sodium, and potassium chlorides on the interplanar spacings in 5:1 water-clay systems are shown in Figures 5, 6, and 7. Normalities are based on the total water present.

Increasing concentrations of lithium chloride reduce the (001) spacings in a regular manner until, at 1.07N, a minimum of 20.5 Å is reached.

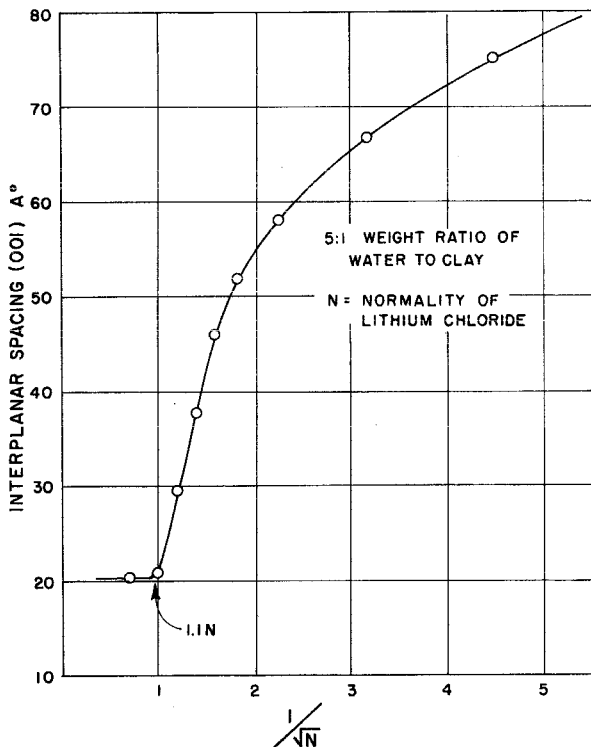


FIGURE 5. — Lattice expansion of lithium montmorillonite in lithium chloride solutions.

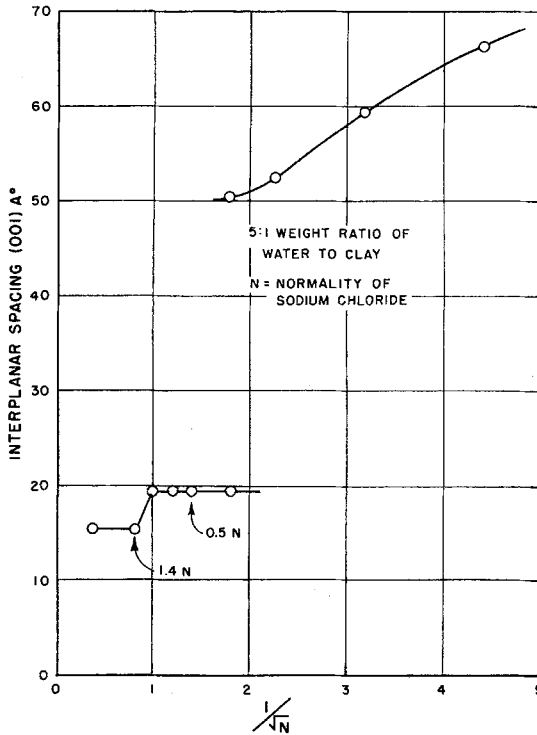


FIGURE 6. — Lattice expansion of sodium montmorillonite in sodium chloride solutions.

As sodium chloride is added, continuous lattice shrinkage occurs to about 50 Å, followed by a discontinuous decrease to 19.2 Å between 0.2N and 0.5N. A further collapse to 15.6 Å appears at 1.4N.

No resolvable high spacings are observed for the potassium clay and a weak 15.6 Å reflection is present even at 0.05N potassium chloride. Its intensity steadily increased until a maximum is reached at about 0.14N. No other changes are observed at higher concentrations.

PART II — RHEOLOGICAL STUDIES

INTRODUCTION

A considerable number of experimental investigations have been conducted on the electrolyte-viscosity relationships of the montmorillonite group, and informative bibliographies have been compiled (Hauser, 1945, p. 287; Marshall, 1949, p. 152). These surveys reflect the considerable discussion and controversy that exists regarding its rheology, particularly in water suspensions, and the difficulties with terminology that have arisen

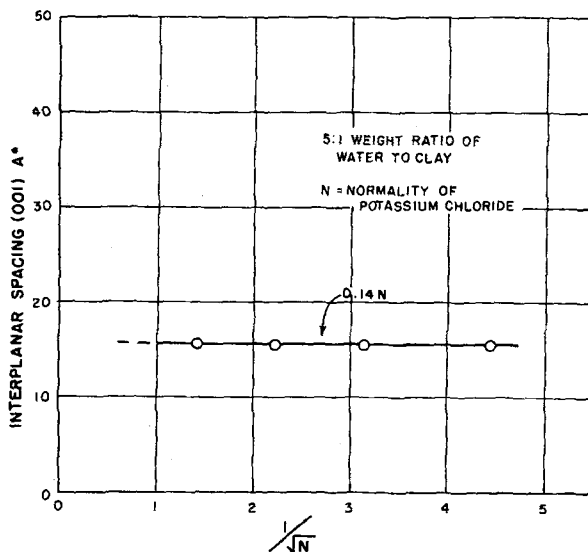


FIGURE 7.— Lattice expansion of potassium montmorillonite in potassium chloride solutions.

in describing the dispersion-agglomeration transition. Although the complex rheological behavior of clay suspensions is generally recognized, single apparent viscosities, *e.g.*, quantities derived from single shear rate or shear stress measurements, have been used to describe their rheological behavior. In certain of the studies involving multiple shear rate-shearing stress measurements, the physical significance of the measured quantities is not readily discernible since the data have been expressed in terms which are at variance with some accepted concepts.

In the present study the dispersion-agglomeration transition is expressed in terms of certain ideal rheological models and the degree with which the actual systems approximate the ideal cases is analyzed. Rheological measurements were obtained with a recording Couette-type viscometer designed to provide a wide spectrum of shear rates and shearing stresses and supplemented with measurements of the filtration changes which accompany the transition and the X-ray diffraction experiments described in Part I of this paper.

EXPERIMENTAL METHODS

Preparation of Montmorillonite Suspensions

Stock suspensions of each of the montmorillonite salts described in Part I were prepared by dispersing the dry clay material in distilled water and aging the system in a roller oven at 76.6° C for 72 hours. A second uniform aging for 16 hours at 76.6° C was used for the pure clay-water and clay-water-electrolyte systems prepared from these stock suspensions,

the latter being prepared by addition of electrolyte to pure clay-water systems. Normalities of the added electrolyte are based on the total water present.

Rheological Measurements

Variable speed outer cylinder rotation was provided by a continuously variable (0-1100 rpm) transmission. A beryllium-copper spring constituted the torque restoring unit, rapid and automatic pick-up of the bob deflection being achieved by means of an ultra-low torque indicating potentiometer with the resultant signal being transmitted to a high speed millivolt recorder. The system is enclosed in an insulated constant temperature oil bath with temperature controlled to within $\pm 0.05^\circ \text{C}$. Shear rate-shearing stress ranges of 1600 sec.^{-1} and $200,000 \text{ dyne cm.}^{-2}$, respectively were obtained with various rotor-bob-torsion spring combinations.

Measurements were conducted at 25°C . Shear rate-shearing stress curves were obtained by taking a series of readings, beginning at a high shear rate and decreasing to a fixed level, and repeating the steps in the opposite direction. Where a system exhibited thixotropic behavior the equilibrium method was employed to reduce the influence of the time factor (Fischer, 1950, p. 186).

A measure of thixotropy was obtained using a method similar to that described by Pryce-Jones (1952, p. 104). A high rotor speed was imposed on the sample for several minutes to break down the structure, the rotor then stopped and the sample allowed to rest for a certain period of time. (Rest times of 30, 60, 180, 300, 600, and 900 seconds were used in the measurements reported here.) Then with the drive adjusted to produce a rotor speed of about 3 rpm, rotation was initiated; the maximum deflection recorded was taken as the point of gel rupture and reported as the gel strength for that rest period.

Filtration Measurements

The filtration apparatus used in these measurements is identical to that described in API Code 29. ‡ The test procedure was modified to permit a graphical correction for "initial surge loss" which is included in the standard measurement and which is related to factors other than those governing only constant pressure filtration. Briefly, the test involves subjecting a sample to 100 psi nitrogen pressure and noting the volume of filtrate collected from a standardized cell during certain time intervals. In this study, the results are reported in milliliters, as a "corrected 30 minute water loss."

MATHEMATICAL SECTION

The functional relationship between shear rate and shear stress is referred to as the equation of flow. In the simplest case, that of Newtonian

‡ API Code 29, Third Edition, May 1950, "Recommended Practice for Standard Field Procedure for Testing Drilling Fluids."

flow, these variables are related by a proportionality constant, *i.e.*, the viscosity coefficient. When a dependence on shear rate occurs, the system may be a Generalized Newtonian (Reiner, 1949, p. 52), under which classification is found the pseudoplastic, or the system may be a Bingham Plastic. Working equations for the flow of these two systems in a rotational viscometer are reviewed in the following sections.

All equations are expressed in cgs units but the actual calculations are expressed on the basis of the experimental variables for the viscometer employed in this study, *e.g.*, rotor speed in rpm and recorder reading in millivolts.

Newtonian or Generalized Newtonian Systems

Although not a true rheological equation it is useful as an approximation to express the relationship between the shear rate $\dot{\epsilon}$ and shearing stress p for the non-linear behavior of the Generalized Newtonian system in the form:

$$\dot{\epsilon} = Kp^n \tag{1}$$

When $n=1$ equation (1) becomes the equation of flow for the Newtonian system. Introducing into equation (1) the expressions generally valid for fluid flow between coaxial rotating cylinders and integrating gives:

$$\bar{\omega} = \frac{K}{2n} \left(\frac{T}{2\pi l_b} \right)^n \left(\frac{1}{r_b^{2n}} - \frac{1}{r_c^{2n}} \right) \tag{2}$$

where:

- $\bar{\omega}$ = angular velocity of rotor, rad.per.sec.
- T = torque exerted on bob, dyne cm.
- l_b = height of fluid between rotor and bob, cm.
- r_b = radius of bob, cm.
- r_c = radius of rotor, cm.
- n = index of non-linear behavior
- K = material constant.

Again for $n=1$ equation (2) reduces to the Couette-Margules equation which serves as a check. Equation (2) suggests a method for describing the flow properties of a pseudoplastic. If the exponential law defined by (1) is adequate, data for such a system obtained with different rotor-bob combinations can be plotted as $\log \bar{\omega}$ versus $\log T$ and a family of linear curves with identical slope (n) will result.

Bingham Plastic Systems

The rheological behavior of a Bingham plastic is defined in terms of a plastic viscosity, μ_p , and a yield point, ϕ . The functional relationship between $\dot{\epsilon}$ and p for this system is given by:

$$\dot{\epsilon} = \frac{1}{\mu_p} (p - \phi) \tag{3}$$

Introducing into (3) the expressions generally valid for flow between coaxial rotating cylinders gives the following series of Reiner-Riwlin equations:

For the linear (laminar) flow portion of the $\dot{\epsilon}$ -p curve:

$$\bar{\omega} = \frac{T}{4\pi l_b \mu_p} \left(\frac{1}{r_b^2} - \frac{1}{r_c^2} \right) - \frac{\phi}{\mu_p} \log_e \frac{r_c}{r_b} \quad (4)$$

For the non-linear (plug) flow portion of the $\dot{\epsilon}$ -p curve:

$$\bar{\omega} = \frac{T}{4\pi l_b \mu_p r_b^2} - \frac{\phi}{\mu_p} \left[1 + \log_e \left(\frac{T}{2\pi l_b r_b^2 \phi} \right) \right] \quad (5)$$

The laminar-plug transition critical angular velocity is given by:

$$\bar{\omega}_{pc} = \frac{\phi}{2\mu_p} \left(\frac{r_c^2}{r_b^2} - 1 - 2 \log_e \frac{r_c}{r_b} \right) \quad (6)$$

The intercept on the p axis corresponding to the point where ϕ is initially exceeded is given by:

$$T_o = 2\pi l_b r_b^2 \phi \quad (7)$$

DISCUSSION OF EXPERIMENTAL RESULTS

The Pure Montmorillonite-Water System

Influence of Exchange Ion on Rheological Properties

Typical experimental data for a given rotor-bob geometry demonstrating the influence of the exchange ion in pure montmorillonite-water systems are given in Figure 8. Suspensions of the Li, Na, and K salts, all at the same 1.49 percent by volume solids, exhibit very anomalous flow behavior. Of particular interest is the displacement of these three $\dot{\epsilon}$ -p curves in the order of increasing ionic hydration energy, *e.g.*, K^+ , Na^+ , Li^+ . The lower degree of dispersion of Ca montmorillonite is reflected in its lower degree of anomalous behavior even at more than triple the volume of solids present in the monovalent montmorillonites. The data suggest that increased cation hydration increases the degree of asymmetry of the kinetic unit and the amount of water bound thereto.

The non-thixotropic behavior of pure bentonite has been ascribed (Hauser, 1945, p. 287) to an absence of certain specific ions; these four systems are similarly devoid of thixotropy.

Equation (2) predicts linear logarithmic plots of $\bar{\omega}$ versus T, or their equivalent, $\log \Omega$ (rotor rpm) versus $\log V$ (recorder reading in millivolts). This is substantiated in the data plotted in Figure 9 for three rotor-bob combinations; the curves are linear and have the same slope. Equations (4) and (5) have been found inapplicable, thus ruling out the presence of a Bingham Plastic yield point. The appearance of two linear portions suggests the presence of a separate index of non-linear behavior (n) for each and illustrates the approximation involved in proposing a single exponential

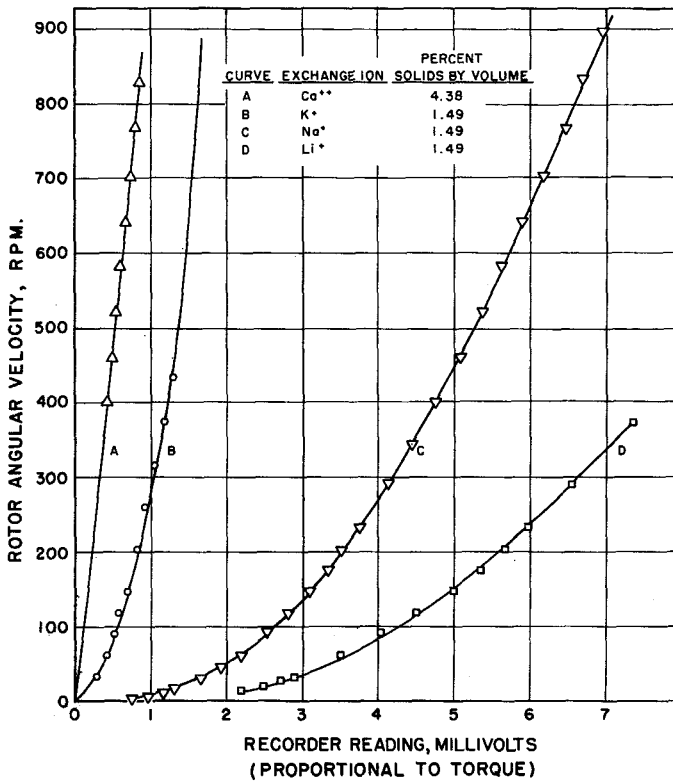


FIGURE 8. — Influence of exchange ion in a pure montmorillonite-water system.

equation. It appears that the rheology of these pure montmorillonite-water systems can be approximately defined in terms of the Generalized Newtonian model (pseudoplastic).

Effect of Solids Concentration on Rheological Properties

The effects of solids concentration on the $\dot{\epsilon}$ - p curve of a pure Na montmorillonite-water system is shown in Figure 10. It was selected because its degree of dispersion is intermediate in the monovalent series. The considerable influence of lamellae asymmetry is clearly evident as the solids concentration increases. Two different slopes for each $\dot{\epsilon}$ - p curve, suggesting a different index of non-linear behavior (n) for the upper and lower ranges, are again evident. This influence is further emphasized in Figure 11 where both (n) values are plotted versus the solids concentration. The single exponential equation, *i.e.*, a single (n) value, appears to be applicable only at 2.88 or less weight percent solids, the slopes increasing very rapidly over a narrow range of solids concentration. Above about 6.5 weight percent solids this system has a consistency resembling that of a thick paste.

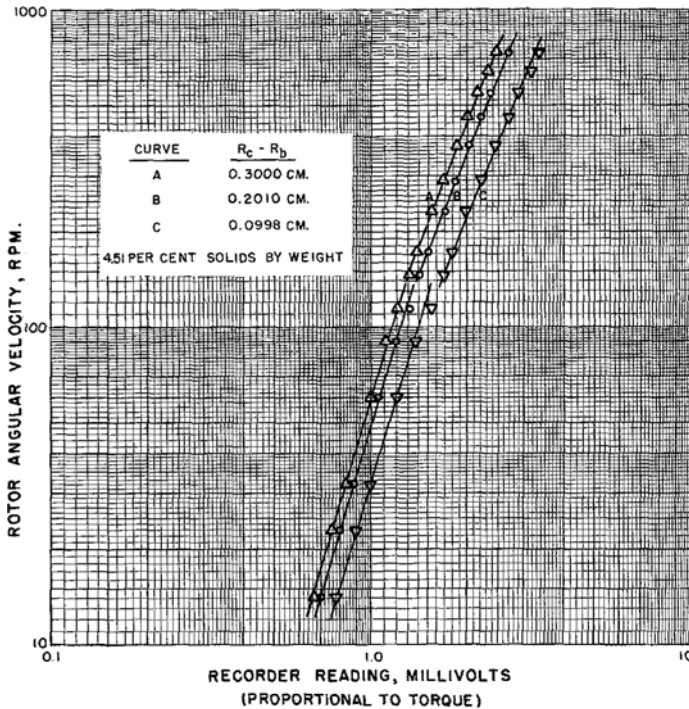


FIGURE 9. — Flow of a pure sodium montmorillonite water system (aged) in a concentric cylinder viscometer.

The Montmorillonite-Water-Electrolyte System

Dynamic Rheological Properties

The effect of gradual electrolyte addition on the dispersion — agglomeration process for the Na montmorillonite system in terms of $\dot{\epsilon}$ - ρ , *e.g.*, rotor speed versus recorder reading, curves are shown in Figures 12 and 13. The rheological transformations occurring in this system are representative of those occurring in all the systems described here. A plastic viscosity in cp and a yield point in $\text{lb. per 100 sq. ft.}$ were calculated from experimental points lying in the linear portion of each curve using equation (4) and the appropriate conversions. Equation (5) predicts a zone of non-linear behavior below a certain critical shear rate. This is substantiated by the agreement between experimental points and calculated non-linear regions, shown as the dotted curves, obtained by substituting the corresponding values of plastic viscosity and yield point in equation (5) using appropriate conversions. Addition of electrolyte complicates low shear rate measurements because such phenomena as syneresis and thixotropy which give rise to slip and long relaxation times, respectively, begin to appear. These data suggest that on addition of electrolyte the rheology of a pure montmorillonite-water

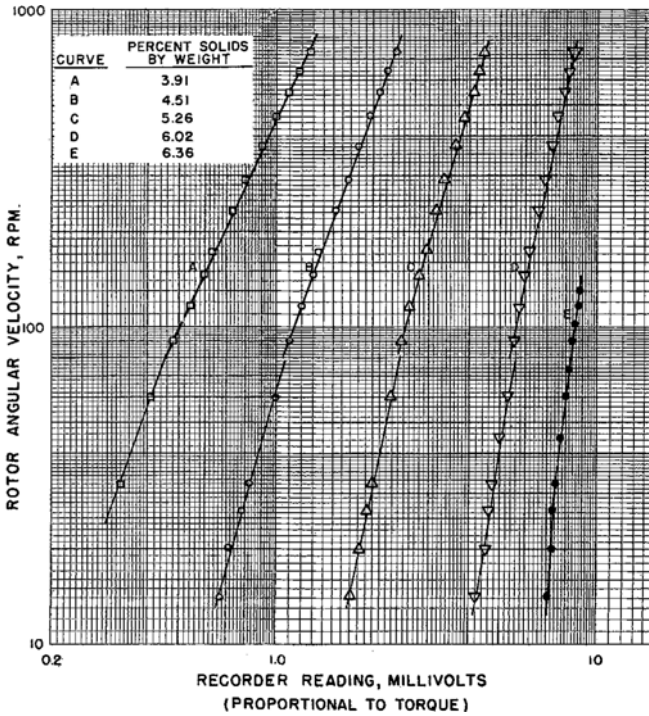


FIGURE 10.—Effect of solids concentration in a pure sodium montmorillonite-water system.

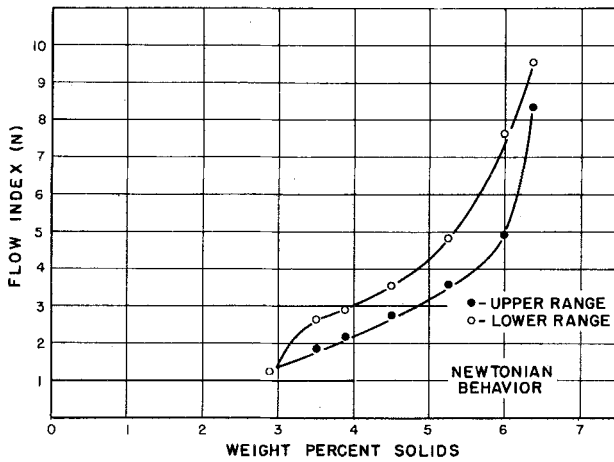


FIGURE 11.—Effect of solids concentration on the flow index of a pure sodium montmorillonite-water system.

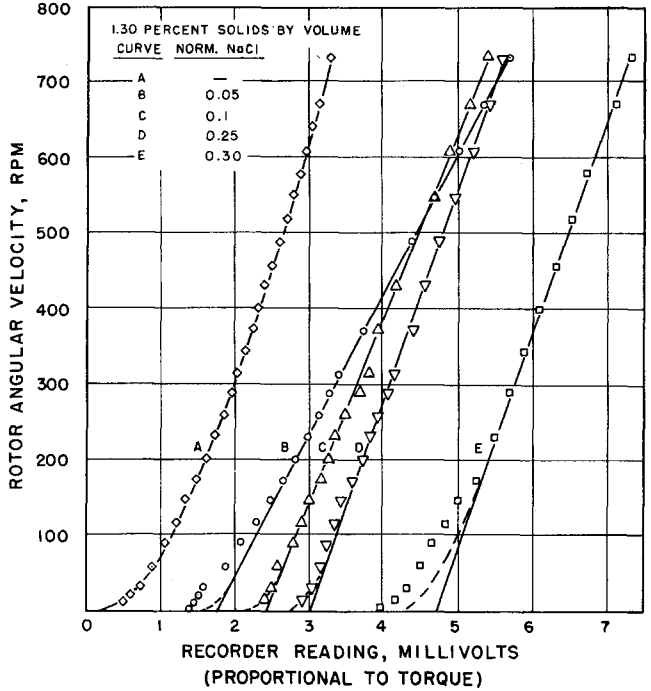


FIGURE 12.—Effect of sodium chloride on the flow properties of a sodium montmorillonite-water system.

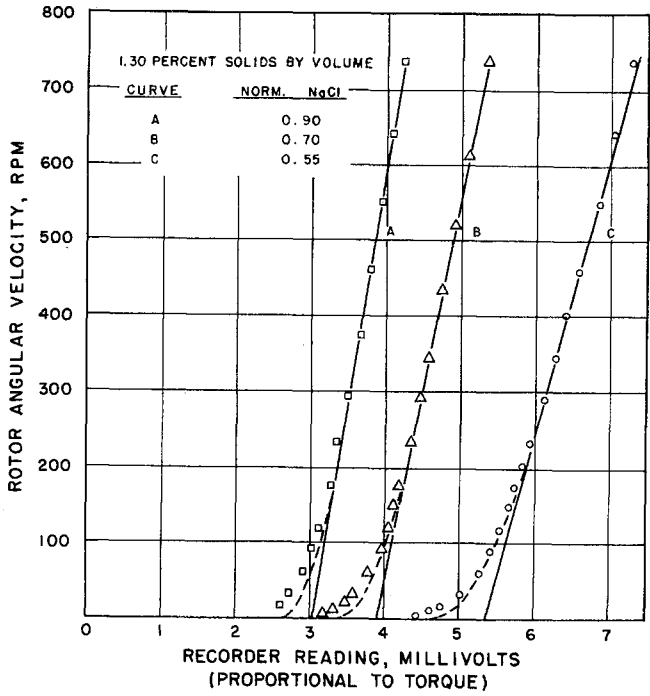


FIGURE 13.—Effect of sodium chloride on the flow properties of a sodium montmorillonite-water system.

system is gradually shifted from Generalized Newtonian behavior to a behavior which is approximately described by the Bingham Plastic model. This shift is accompanied by certain time effects described later.

Figures 14 and 15 illustrate the changes that occur in plastic viscosity and yield point as this shift continues. The order of decreasing hydration energy is again reflected in the relative displacement of the plastic viscosity curves. Marked decreases in plastic viscosity are seen to occur in the highly dispersed Li and Na montmorillonites whereas the changes are smaller for the less dispersed K and Ca montmorillonites. The yield point maxima are thought to be associated with the initial bunching together of individual lamellae into clumps or coacervates, evidence for this being substantiated by the observation that the maxima occur in the region where the X-ray measurements indicate the transition to the lower spacing has been completed. The amplitude and relative displacement of these maxima suggest that the magnitude of the interparticle forces which are reflected in the yield point measurement depends to a large extent on the exchange ion present. It also suggests that coacervating ability increases in the monovalent series with atomic weight, *e.g.*, Li⁺, Na⁺, K⁺, this being the order of decreasing ion hydration.

Data for the Ca salt of montmorillonite are presented for comparison purposes.

Figures 16 and 17 are included to show the effects of different electrolytes on a specific exchange ion, Na⁺ in this case. The degree of base exchange is in each instance determined by a number of factors which were not controlled in these additions; in general, however, the shift from dispersed to coacervated state is accompanied by similar changes in rheological behavior. These data are particularly interesting in that the plastic viscosities tend to gradually approach from a higher level the values for the corresponding systems in which both added ion and exchange ion are identi-

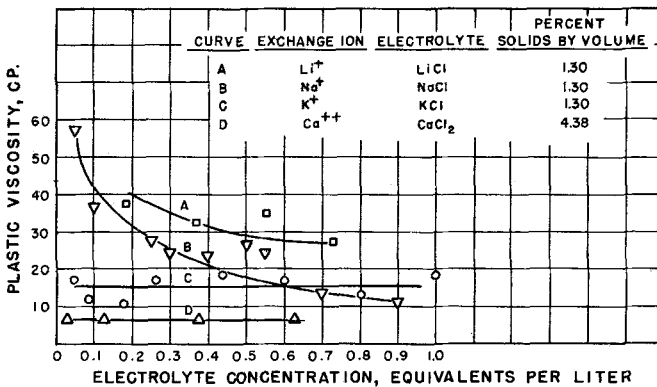


FIGURE 14. — Effect of addition of electrolyte on the plastic viscosity of montmorillonite suspensions.

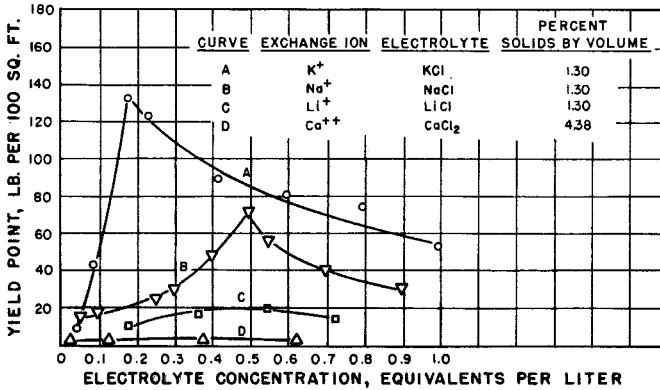


FIGURE 15.—Effect of addition of electrolyte on the yield point of montmorillonite suspensions.

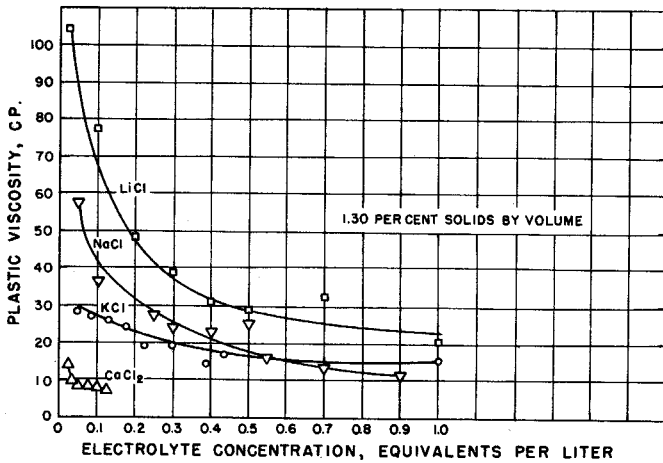


FIGURE 16.—Effect of various electrolytes on the plastic viscosity of a sodium montmorillonite-water system.

cal; the yield point data show a similar trend for KCl additions whereas the data for LiCl additions are consistently higher.

Static Rheological Properties

The shift from dispersed to coacervated state is accompanied by the development of thixotropy. This phenomenon is recognized in a dynamic measurement by the appearance of a hysteresis loop and in a static measurement by the development of a gel structure which increases in strength with increased rest time and which can be repeatedly disrupted by shearing action.

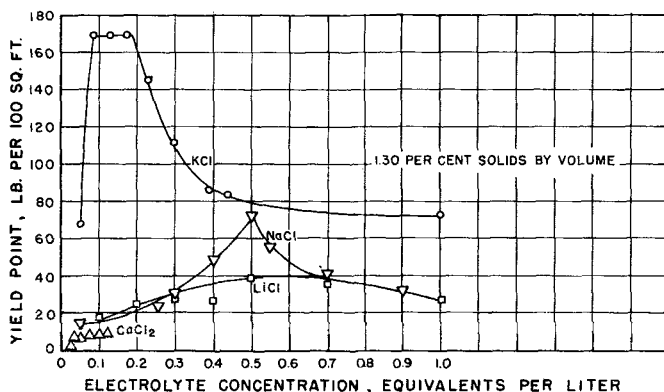


FIGURE 17.— Effect of various electrolytes on the yield point of a sodium montmorillonite-water system.

Since maximum shearing stress is initiated at the wall of the bob it is assumed that a gel will first rupture at this surface, in which case equation (7) is applicable. Using the procedure described earlier, the gel strengths given in Table I were obtained by substituting maximum deflection values in (7) and converting to yield point units of lb. per 100 sq. ft.

TABLE I.— EFFECT OF ADDITION OF ELECTROLYTE ON THE DEGREE OF THIXOTROPY OF MONTMORILLONITE SUSPENSIONS

Exchange ion	Electrolyte	Electrolyte concentration equiv. per liter	Gel strength, lb. per 100 sq. ft.					
			Rest time (sec.)					
			30	60	180	300	600	900
Li ⁺	LiCl	0.183	—	20.7	23.6	26.6	31.0	33.0
		0.367	25.1	26.6	33.5	37.9	41.4	42.8
		0.550	30.0	30.5	38.4	43.3	46.3	52.2
		0.733	19.7	25.1	28.6	33.5	37.9	40.4
Na ⁺	NaCl	0.05	17.5	19.7	23.1	25.6	28.6	29.5
		0.10	19.0	19.9	23.2	25.9	28.9	29.9
		0.25	29.1	33.9	40.0	41.7	41.1	50.0
		0.30	33.9	36.9	42.5	45.8	51.3	53.1
		0.40	36.2	39.3	44.2	46.7	50.1	52.5
		0.50	64.5	65.0	67.4	68.0	68.0	68.0
		0.55	51.0	52.2	55.8	57.6	60.4	63.5
		0.70	35.7	35.3	37.1	38.6	37.7	42.5
K ⁺	KCl	0.0438	8.2	12.3	18.4	20.0	23.4	24.7
		0.088	40.4	45.1	50.3	52.7	57.8	60.7
Ca ⁺⁺	CaCl ₂	0.025	2.1	2.6	3.1	2.9	3.7	3.9
		0.125	3.1	3.3	3.9	4.6	4.7	4.1
		0.375	2.7	2.8	4.5	4.9	5.6	5.6
		0.625	2.3	2.9	4.0	4.1	4.7	5.0

The data exhibit trends which reflect the yield point variations shown in Figure 15. The occurrence of maxima followed by less buildup in gel strength during any given time suggests that the appearance of thixotropy is favored by a narrow range of coacervate interaction energies.

Although the method employed is very useful, only a qualitative indication of thixotropy should be inferred from these data; Hookean behavior and an absence of slip are assumed whereas the rupture point as measured here appears to be a function of shear rate and the nature of the rotor-bob surfaces, the latter apparently being due to slip. This effect becomes more pronounced as the system shifts toward coacervation, proving most troublesome in this investigation in the K montmorillonite-water-KCl system.

The data in Table II are included to demonstrate the effects of different electrolytes on the degree of thixotropy of the Na salt of montmorillonite. The degree of thixotropy appears to be consistently greater over the corresponding systems in which both exchange ion and added ion are identical.

Filtration Properties

The data presented in Figure 18 illustrate that small changes in electrolyte concentration have a large effect on filtration properties.

TABLE II. — EFFECT OF VARIOUS ELECTROLYTES ON THE DEGREE OF THIXOTROPY OF A SODIUM MONTMORILLONITE-WATER SYSTEM

Electrolyte	Electrolyte concentration equiv. per liter	Gel strength, lb. per 100 sq. ft.					
		Rest time (sec.)					
		30	60	180	300	600	900
LiCl	0.05	11.5	13.3	19.6	20.6	24.5	26.2
	0.10	15.2	18.9	22.7	24.2	26.1	28.3
	0.20	29.0	29.9	26.3	38.6	40.8	42.0
	0.30	30.4	32.6	36.3	39.2	41.7	43.4
	0.40	33.3	35.6	38.4	41.8	45.6	47.5
	0.50	47.0	49.9	54.3	56.5	57.3	59.7
	0.70	40.4	45.4	47.5	49.9	53.0	54.4
	1.00	24.6	26.7	30.0	34.5	41.9	41.9
KCl	0.018	—	14.8	16.7	20.7	22.2	26.6
	0.053	70.9	69.9	85.2	94.5	101.4	106.9
	0.088	145.8	152.8	165.9	170.9	173.3	189.6
	0.131	122.1	126.5	139.3	128.5	143.8	159.5
	0.175	111.8	116.7	117.7	116.2	121.6	121.6
	0.228	103.9	103.9	103.9	103.9	103.9	103.8
	0.298	76.3	74.8	75.8	79.8	81.7	85.2
	0.385	49.0	50.2	51.7	52.7	53.2	54.7
0.438	54.2	54.2	55.1	56.1	58.1	57.6	
CaCl ₂	0.035	6.1	6.5	7.0	7.2	8.3	8.7
	0.050	6.4	6.6	7.0	7.6	8.4	9.3
	0.075	6.7	7.0	7.6	8.8	9.2	9.3
	0.100	7.3	7.5	8.2	8.6	9.5	9.6
	0.125	6.5	6.9	7.2	7.5	8.4	8.8

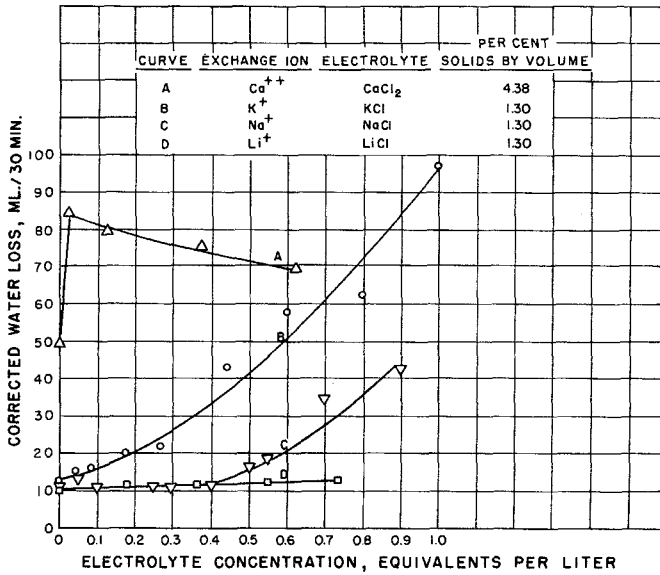


FIGURE 18.— Effect of addition of electrolyte on the filtration characteristics of montmorillonite suspensions.

In the range of concentrations employed the tendency is for cake resistance § to decrease in the monovalent series with the shift from dispersed to coacervated state. Addition of Ca⁺⁺ tends to produce a minimum in cake resistance. The relative displacement of the curves is attributed to water associated with the clay, the order being that of increasing ion hydration. A bunching together of individual lamellae into clumps or agglomerates should tend to produce a filter cake containing large voids between coacervates, the net result being an increased water loss. Recalling that the yield point maxima are thought to be associated with the formation of these units, the sharp increases in filtration rate shown by the K and Na systems in the region of the yield point maxima suggest that beyond this point these voids actually form upon filtration. Thus filtration becomes more dependent on this type of induced porosity and less dependent on ion hydration. This is supported by the absence of a well defined yield point maximum for the Li system and concurrently a smaller increase in water loss.

The apparent decrease in water loss for the Ca system can be explained in part on the basis of a consolidation by rearrangement of the coacervates.

Figure 19 is included to show the effects of different electrolytes on the filtration characteristics of the Na system; the overall effect appears to be a slightly higher water loss which gradually approaches the values for the corresponding systems in which exchange ion and added ion are identical.

§ The resistance of a filter cake to flow of filtrate.

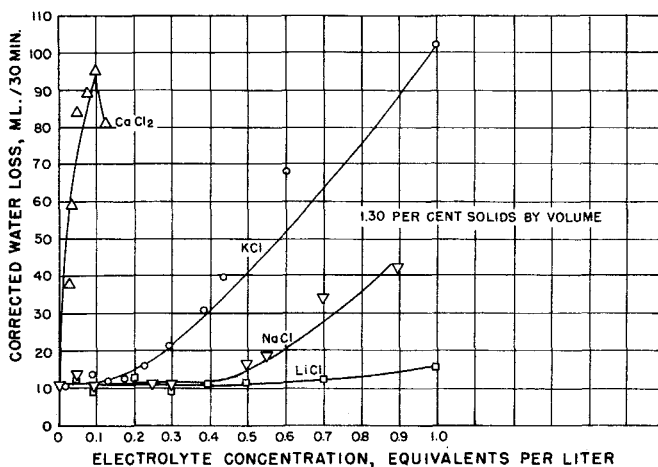


FIGURE 19.— Effect of various electrolytes on the filtration characteristics of a sodium montmorillonite-water system.

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REFERENCES

- Bradley, W. F., Grim, R. E., Clark, G. L. (1937) *A study of the behavior of montmorillonite upon wetting*: Z. Krist., vol. 97, pp. 216-222.
- Collis-George, N., Bodman, G. B. (1954) Proceedings of the 1954 Pacific Coast Regional Conference on Clays and Clay Technology (to be published).
- Fischer, E. K. (1950) *Colloidal dispersions*: John Wiley and Sons, Inc., New York.
- Hauser, E. (1945) *Colloid chemistry of clays*: Chem. Rev., vol. 37, pp. 287-321.
- Hofmann, U., Bilke, W. (1936) *Über die innerkristalline quellung und das basenaustauschvermögen des montmorillonits*: Kolloid Z., vol. 77, pp. 239-251.
- Hofmann, U., Endell, K., Wilm, D. (1933) *Kristallstruktur und quellung von montmorillonit*: Z. Krist., vol. 86A, pp. 340-347.
- Marshall, C. E. (1949) *The colloid chemistry of the silicate minerals*: Academic Press, Inc., New York.
- Mering, J. (1946) *On the hydration of montmorillonite*: Trans. Farad. Soc., vol. 42B, pp. 205-219.
- Pryce-Jones, J. (1952) *Studies in thixotropy*: Kolloid Z., vol. 129, pp. 96-122.
- Reiner, M. (1949) *Deformation and flow*: H. K. Lewis and Co., Ltd., London.