VISCOSITY STUDIES ON DILUTE CLAY MINERAL SUSPENSIONS

By

W. H. Wood and W. T. Granquist[1]
The Floridin Company, Tallahassee, Florida

AND

I. M. Krieger
Case Institute of Technology, Cleveland, Ohio

ABSTRACT

A technique has been developed for obtaining reproducible viscometric data on dilute clay suspensions using the recently developed capillary viscometer of Maron, Krieger and Sisko. Aging and type of mixing have important effects on the viscosity of the dispersions. Attapulgite, hectorite, and Wyoming bentonite exhibit non-Newtonian behavior at all concentrations studied. The effect of temperature on the reduced fluidities of suspensions of the three clays is negligible. In this respect they agree with the behavior predicted for suspensions of rigid, noninteracting particles.

INTRODUCTION

The naturally occurring clay minerals differ widely in the properties of their aqueous dispersions. The so-called "gel-forming" clays form stable, highly viscous suspensions at fairly low concentrations, while others require much higher contents of solids to reach comparable viscosities. Although several important uses of the gel-forming clays depend on their ability to form viscous suspensions, the mechanism of the thickening action is not well understood. The present study is directed toward elucidation of the relation between structure, particle shape and electrical charge of the clay on the one hand, and the viscosity of its dispersions on the other.

The most widely used gel-forming clays are Wyoming bentonite, hectorite and other montmorillonite varieties, and attapulgite. Several viscometric studies on bentonite have been reported in the literature (Scott Blair and Crowther, 1929; Ambrose and Loomis, 1933; Rossi, 1941; Mukherjee, Sen Gupta, and Sen, 1942; Erbring, Broese, and Bauer, 1943), describing measurements made with different types of viscometer. From these reports it may be concluded that bentonite suspensions are non-Newtonian and thixotropic, exhibiting yield points at the higher concentrations. It may also be inferred that careful attention must be paid to preparation of the suspensions, choice and operation of the viscometer, and interpretation of the data if the results are to be reproducible and meaningful.

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[1] Present address: Mellon Institute for Industrial Research, Pittsburgh, Pennsylvania.

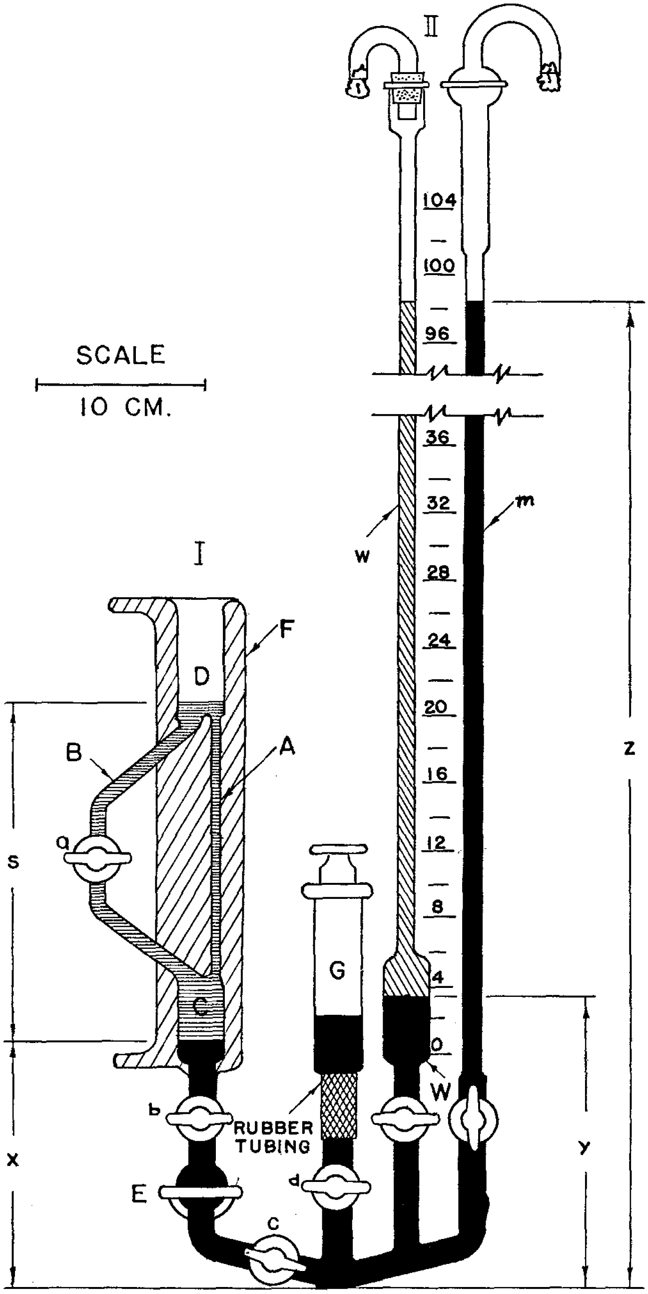

Figure 1. — The viscometer.

SELECTION OF THE VISCOMETER

In measuring the flow behavior of non-Newtonian fluids, the usual objective is to describe the manner in which the viscosity varies with the shear stress or the rate of shear. To accomplish this purpose an absolute instrument is required which permits variation of the shear stress over the desired range. The most widely employed absolute viscometers have been capillary and rotational instruments. Many investigators have favored rotational instruments of the concentric cylinder type, largely because the shear stress in such an instrument is nearly constant throughout the fluid, while in capillary viscometers the shear stress varies from zero at the axis to a maximum value at the tube wall. However, two important studies of the capillary viscometer have removed the difficulties in interpretation which arose from the variation of shear stress, and have permitted the exact calculation of the viscosity at each shear stress. In the first of these studies, Reiner (1949) showed that the relation between apparent viscosity and shear stress is independent of the dimensions of the capillary viscometer, while the second study (Rabinowitsch, 1929), provided a simple method for calculating the true viscosity from the apparent viscosity.

For this study of dilute clay suspensions, the capillary viscometer recently described by Maron, Krieger and Sisko (1954) was selected. This instrument (Fig. 1) provides a continuous range of shear stresses from more than 1000

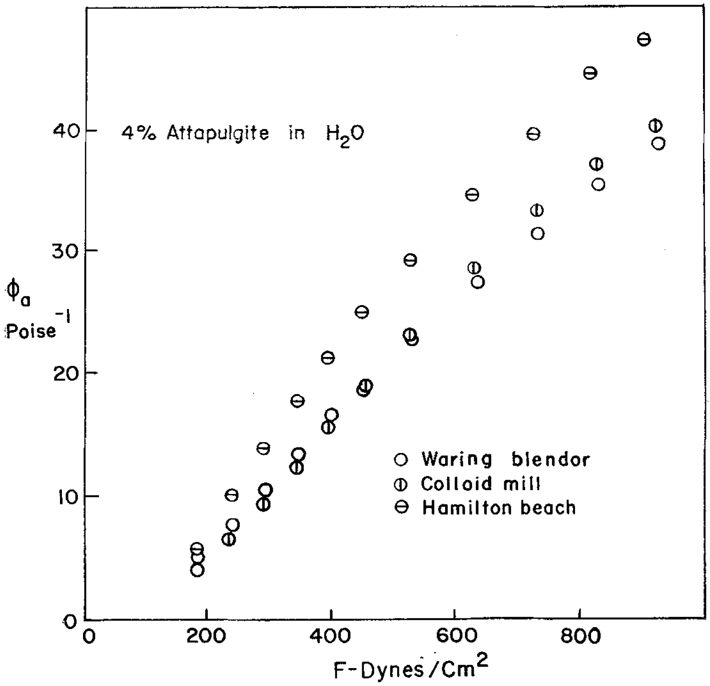

FIGURE 2. — Comparison of results of different types of mixing.

dynes/cm^2 down to zero during a single determination. A feature of this instrument which makes it particularly appropriate for measurements of dilute clay suspensions is the side-arm which by-passes the capillary. Using the hypodermic syringe as a pump, the sample may be agitated before each measurement by forcing it back and forth through the side-arm, thus counteracting any tendency to settle or set up a gel structure.

USE OF THE VISCOMETER

The capillary unit *I* and the manometer unit *II* are clamped together at the ball joint *E*, and water of the desired temperature is pumped through the water jacket *F* from a thermostat. The manometer fluid is pumped up in the appropriate manometer column with the hypodermic syringe *G*, and the stopcock at the bottom of the manometer closed. With stopcocks *a*, *b*, *c* and *d* open, the suspension, which has previously been mixed and brought to temperature, is poured

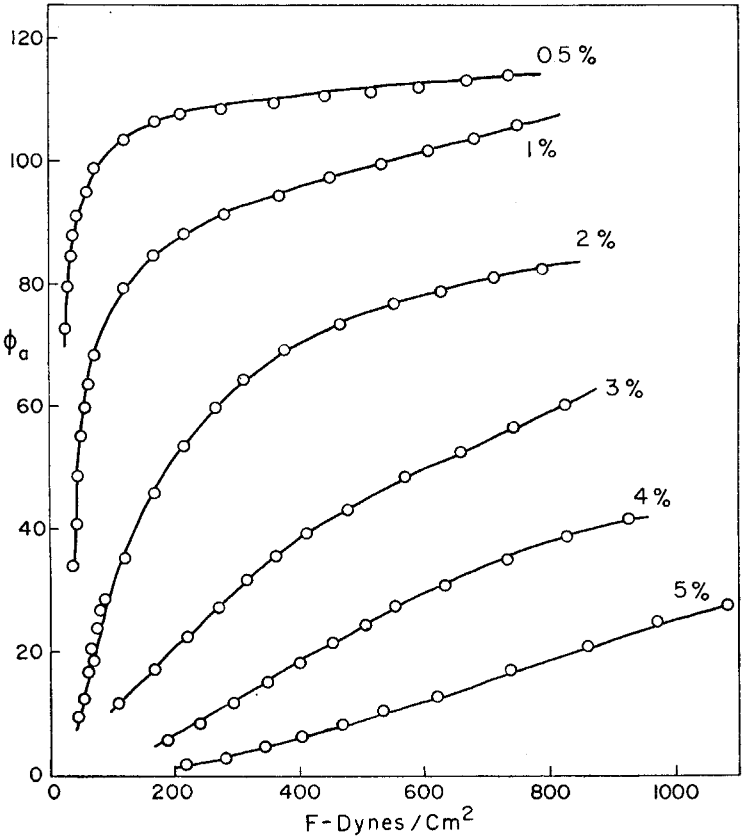

Figure 3. — Concentration study of fluidities of attapulgite suspensions in water at 30° C.

through bulb *D* into bulb *C*. By manipulating the syringe, the sample is pumped several times through side-arm *B*, stopcocks *a* and *d* are closed with the mercury level within bulb *C*, and the manometer stopcock opened. The times *t* at which the falling meniscus passes predetermined heights *z* are measured, using a stopwatch with a split-second hand.

The mercury from the manometer enters bulb *C*, forcing the sample through capillary *A* into bulb *D*, whose radius is the same as that of *C*. The unbalanced pressure across the capillary is measured by the manometer height, while the rate of fall measures the rate of flow. After the desired shear-stress range has been covered, stopcock *a* is opened, and the height z_0 at hydrostatic balance recorded. The sample is then agitated again by repeated passage through the side-arm, the manometer again pumped up, and the entire measurement repeated several times until reproducible results are obtained.

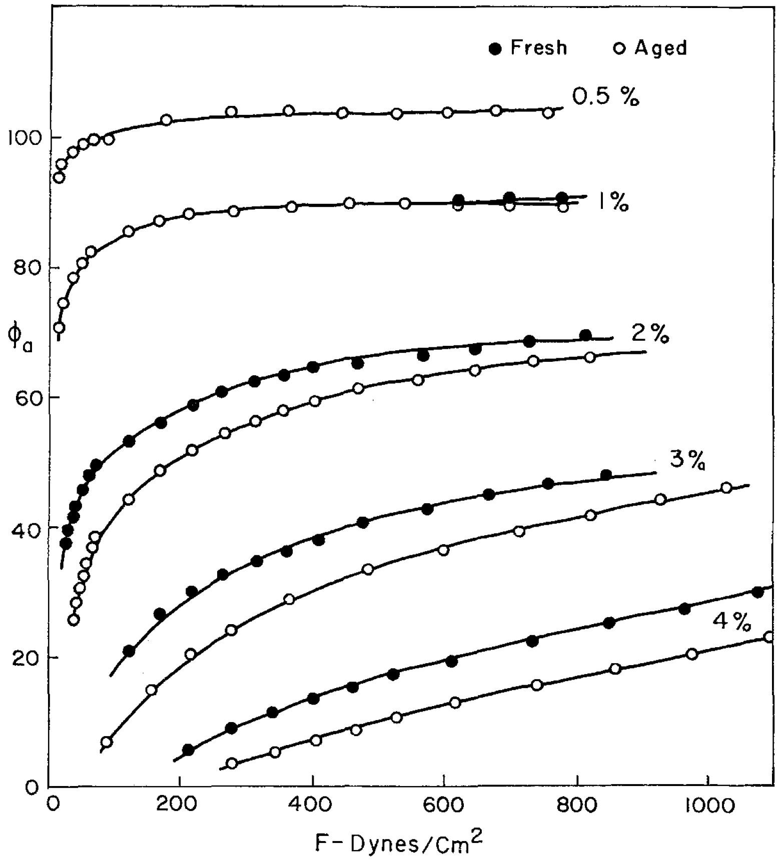

FIGURE 4.—Fluidities of hectorite suspensions at 30° C.

Three different capillary tubes, each about 15 cm long but of different radii, were used in this study. Mercury is the fluid in manometer m, while in manometer w water is used above the mercury to provide a lower pressure range. For a given sample, a capillary unit is selected which gives an experimental time of two to four minutes—long enough for reasonable accuracy but short enough to avoid settling or build-up of structure.

TREATMENT OF DATA

The experimental data are used to calculate the apparent fluidity ϕ_a as a function of the shear stress F. According to Reiner (1949), all capillary data for the same sample should be superposable on this basis. Fluidity, which is the reciprocal of viscosity, is used in this study because the viscosity apparently approaches infinity at low shear stresses, whereas the fluidity approaches zero. Since the general theory of handling data for non-Newtonian fluids is described in the literature, and the theory of this instrument has been reported in detail by Maron, Krieger and Sisko (1954), only the essential steps in the calculation of apparent fluidity and shear stress are reproduced here.

Symbols:

R	radius of capillary
L	length of capillary
Q	volume rate of flow
P	viscous pressure drop across capillary
ρ_m	density of mercury
g	acceleration of gravity
r_m	manometer radius
R_c	radius of bulb C
ρ_s	density of sample

Instrumental constants:

$$\alpha = P/h = \rho_m g\ (1 + r_m^2/R_c^2) \qquad \text{(Manometer factor)}$$

$$B = \frac{8(2.303)Lr_m^2}{\alpha R^4} \qquad \text{(Capillary factor)}$$

$$\gamma = \frac{1.12\ R^4\ \alpha}{64\ L^2} \qquad \text{(Kinetic energy correction factor)}$$

Equations used:

$$\phi_a = \frac{8LQ}{\pi R^4 P} = -B\frac{d\log_{10}h}{dt} \qquad \text{(Apparent fluidity)}$$

$$F = RP/2L = (R\alpha/2L)h \qquad \text{(Shear stress)}$$

$$\phi_r = \phi_a/\phi_{\text{water}} \qquad \text{(Reduced fluidity)}$$

The experimental data, giving h vs. t, are converted to apparent fluidity vs. shear stress by means of equations listed above. In the derivation of these equations it has been assumed that the entire pressure drop across the capillary is due to viscous forces. Under conditions of rapid flow, however, a fraction ϵ

of the pressure is used to accelerate the liquid as it enters the capillary; this fraction is given by: $\epsilon = \gamma \rho_s \phi_a{}^2 h$
The corrected shear stress is obtained by multiplying the uncorrected value by the factor $(1-\epsilon)$, while the corrected apparent fluidity is given by dividing the uncorrected apparent fluidity by the same factor. This "kinetic energy correction" was applied whenever it was large enough to be significant.

EFFECTS OF MIXING AND AGING

In order to prepare dispersions on which reproducible measurements could be made, several methods of mixing the clay with water were studied. A Hamilton Beach mixer, a Waring Blendor, and a Manton-Gaulin colloid mill were used to prepare attapulgite suspensions of various concentrations, and the viscometric behavior of the suspensions studied in the viscometer. Figure 2 typifies the results of this mixing study. It is evident that the dispersions prepared using

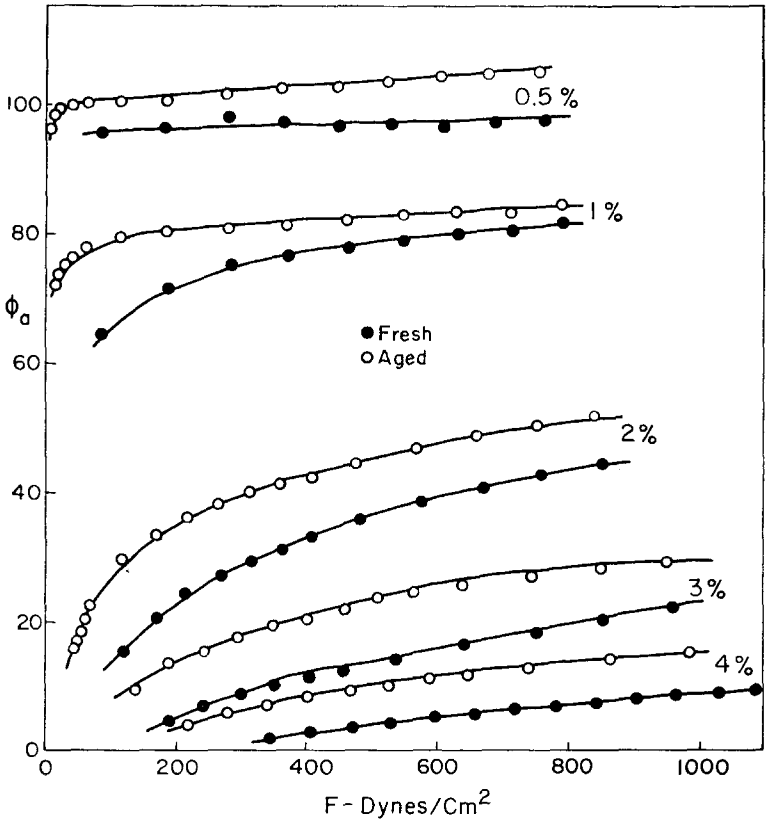

FIGURE 5.—Fluidities of Wyoming bentonite suspensions at 30° C.

the Hamilton Beach mixer are more fluid than those prepared by the other two methods, and that the Waring Blendor and colloid mill results agree fairly well with each other. It was noted that attapulgite samples which had been put through an extrusion process prior to grinding gave different results from the unextruded samples when mixed in the Hamilton Beach mixer, but gave results identical with the unextruded samples when the suspensions were prepared in the Waring Blendor. From these observations it was concluded that the degree of dispersion is higher in the Waring Blendor than in the Hamilton Beach mixer, and hence the Blendor was used in preparing all samples for this study.

Some of the clay suspensions showed a drift in ϕ_a which persisted for as long as a week after they were prepared. Hectorite and some attapulgite samples decreased in ϕ_a, while Wyoming bentonite samples increased. The drop in fluidity of attapulgite samples has been correlated with free moisture content; samples having adequate free moisture show no change on aging. The behavior of the Wyoming bentonite is puzzling, and no explanation has been proved as yet. The aging effect is more rapid at higher temperatures. All samples reported in this study were aged at 50° C until no further drift in fluidity was noted. Seventy-two hours aging proved sufficient in all cases. Aged and freshly-prepared samples are compared in Figures 4 and 5.

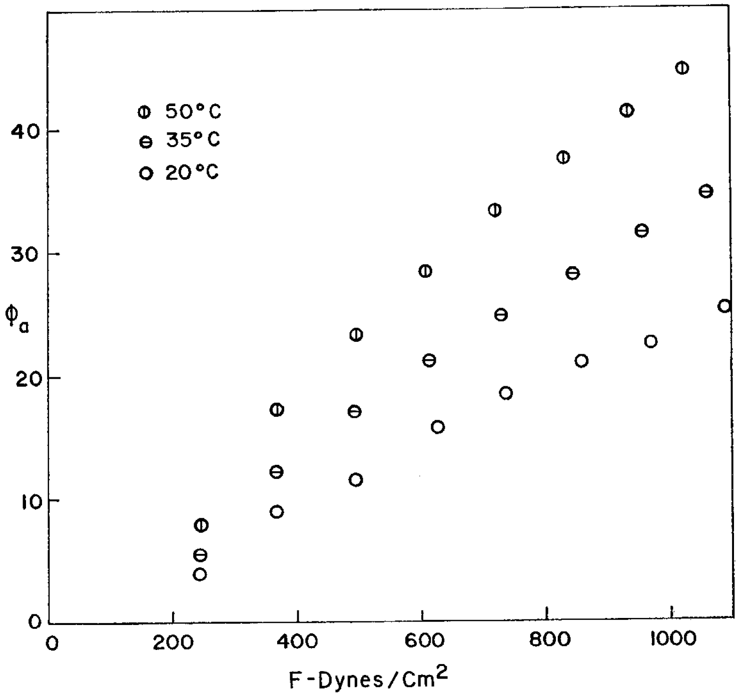

Figure 6. — Effect of temperature on fluidities of 5 percent attapulgite suspensions in water.

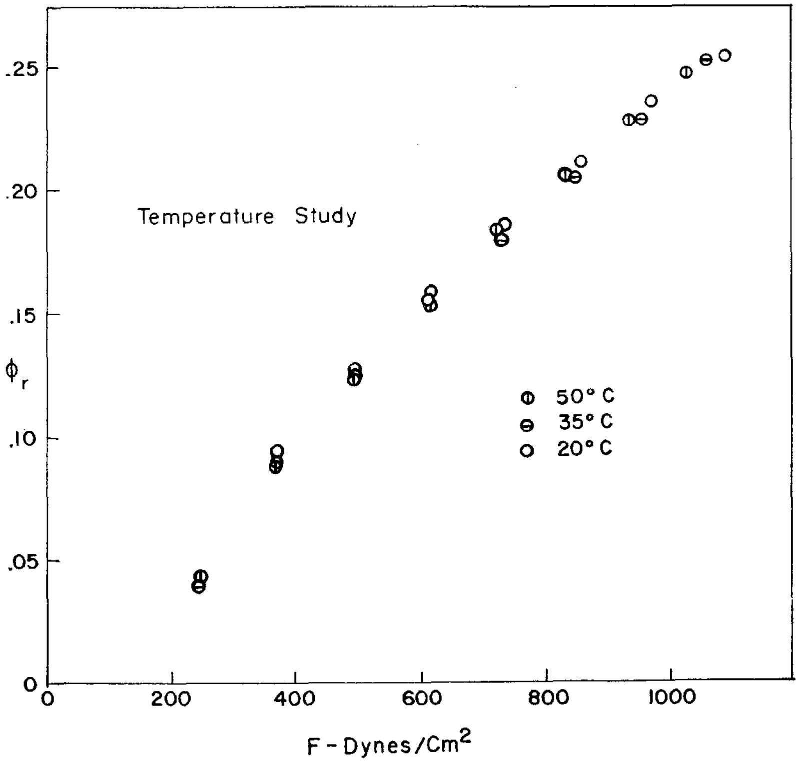

FIGURE 7. — Reduced fluidities of 5 percent attapulgite suspensions.

CONCENTRATION AND TEMPERATURE EFFECTS

The fluidities of attapulgite suspensions from 0.5 to 5.0 percent by weight were studied at 30° C and at shear stresses from 10 to 1000 dynes/cm^2. (The water manometer was used for shear stresses below 100 dynes/cm^2.) The results (Fig. 3) show that attapulgite suspensions are non-Newtonian at all concentrations, exhibiting a rapid decrease in fluidity as the shear stress approaches zero. Similar behavior is observed with hectorite and Wyoming bentonite (Figs. 4 and 5).

Increasing the temperature of measurement decreases the fluidity of the suspension, as is shown for attapulgite by Figure 6. When, however, the apparent fluidity is divided by the fluidity of water at the temperature of measurement, the resulting "reduced fluidity," ϕ_r, becomes independent of temperature, as is shown in Figure 7. Figure 8 presents the reduced fluidities of hectorite and Wyoming bentonite; here again the effect of temperature is small. The theory of the viscosity of dilute suspensions of rigid, noninteracting particles (Simha, 1940; Hermans, 1953) predicts the independence of reduced fluidity, whereas the inclusion of electrical interactions or reversible swelling in the theory would

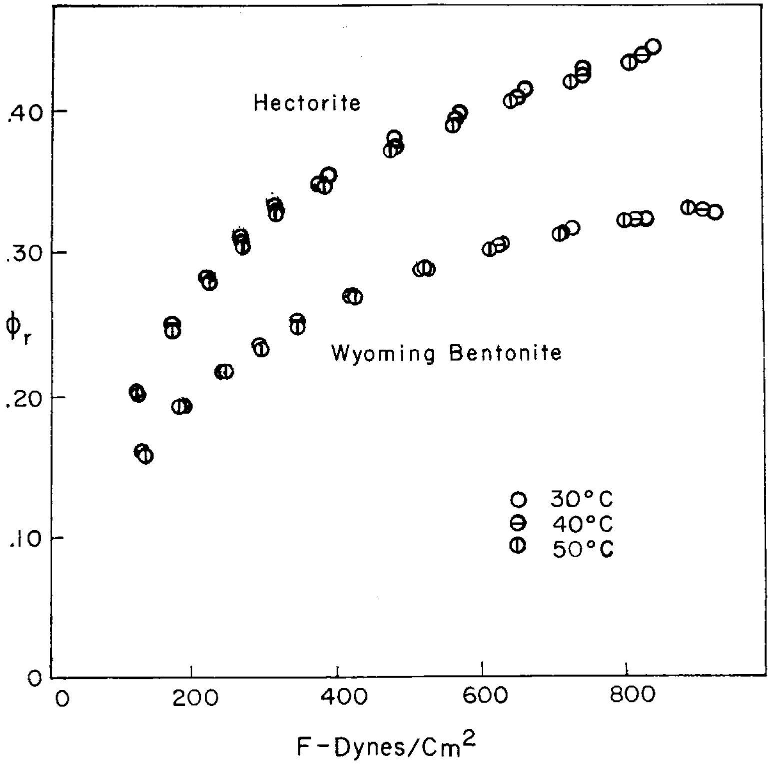

Figure 8. — Reduced fluidities of 2.5 percent hectorite and Wyoming bentonite suspensions.

introduce a temperature dependence. This line of reasoning suggests strongly that the viscosity of dilute clay suspensions is governed by the geometry of the particles rather than by specific interactions between particle and solvent or between particle and particle.

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