

ELECTROKINETIC EFFECTS IN KAOLIN-WATER SYSTEMS. I. THE MEASUREMENT OF ELECTROPHORETIC MOBILITY

by

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ABSTRACT

A NEW apparatus for the measurement of electrophoretic mobilities of particles in concentrated suspensions has been developed. The usual techniques for the study of electrophoretic mobility, such as the microelectrophoretic method and the moving-boundary method, are in general not applicable to suspensions more concentrated than about 1% by volume of dispersed phase, nor are they readily applied to suspensions of particles having an appreciable sedimentation velocity. The new apparatus, which employs an improved design of mass-transport cell, has been used to study suspensions containing up to 50% by volume of dispersed phase. Gravitational effects are eliminated by continuous rotation of the cell during a mobility determination.

Data on kaolin-water systems are presented to illustrate the experimental technique and precision of the measurements. These data are also used to show the relation between the salt flocculation value of a suspension and its electrophoretic mobility.

INTRODUCTION

ELECTROKINETIC effects in disperse systems have been investigated by a variety of techniques including electroosmotic pressure and flow, streaming potential, sedimentation potential and electrophoresis. The principles involved in the use of these procedures have been reviewed by Overbeek (1952) and by the present authors (1965), among others. The commonly employed techniques are limited, however, in that they are adapted to relatively narrow ranges of particle concentration, i.e. highly concentrated porous plugs in the case of electroosmosis and streaming potential, and very dilute suspensions (<1% by volume) in the case of electrophoretic mobility determinations. Furthermore, the theoretical interpretation of electrokinetic effects in terms of an electrokinetic or zeta potential is applicable only to very dilute suspensions, as current theories all use the model of an isolated particle in an infinite medium. The present series of investigations is directed toward elucidating the influence of electrokinetic potential on such bulk physical properties of concentrated suspensions as rheology and stability

to electrolytes, wherein particle interactions are of primary importance. To carry on this work it was necessary, therefore, to develop appropriate means for measuring the electrophoretic mobility of particles in concentrated suspensions.

The technique and apparatus developed are based on the Hittorf method, which is mentioned in several books on colloid science but has seldom been used; Overbeek (1952) cites only Paine (1928), Pauli (1928), and Tattje (1942). In this method, a known potential gradient is applied to a suspension for a certain time, and the amount of material transferred into a collection chamber is determined by a suitable means, e.g. gravimetrically. The apparatus used by these earlier workers required large amounts of suspension and was not suitable for systems containing relatively coarse particles; the apparatus described here, which we call the electrophoretic mass-transport cell, was designed to overcome these difficulties.

DESCRIPTION OF THE MASS-TRANSPORT CELL

The cell in its initial form has been described previously by Sennett and Olivier (1965); a modified cell design has been reported by Long and Ross (1965), who verified the accuracy of the mass-transport technique by comparison of results with those obtained by use of the Burton cell moving boundary method. Long (1965) used the mass-transport cell in an investigation of the effects of particle interactions on electrophoretic mobility.

The cell in its present form is shown in Fig. 1. It consists of three main parts, which are of circular cross-section; a reservoir, filling plug, and collection chamber. The cell is constructed of an acrylic plastic and can be completely disassembled for easy cleaning. Metal electrodes are located on the

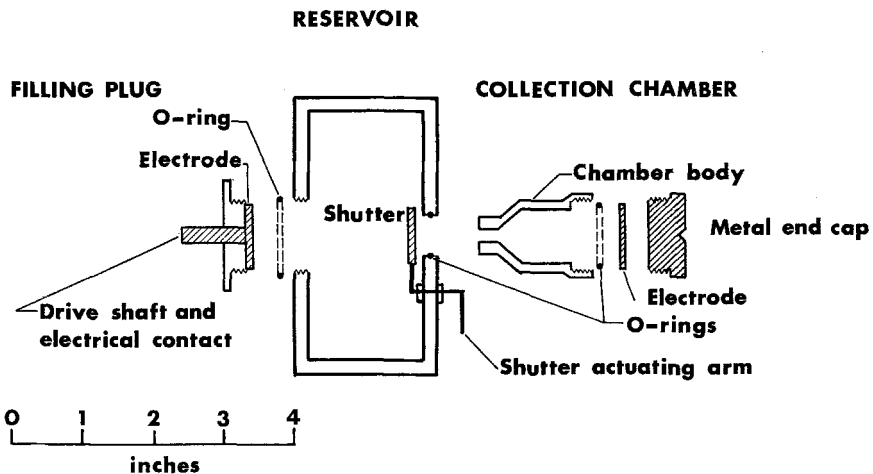


FIG. 1. An exploded view of the component parts of the mass-transport cell.

inside end of the filling plug and at the base of the collection chamber. The complete instrument is shown in the photograph (Plate 1). It is primarily a wide-range, constant-current power supply with meters for indicating applied current and voltage, and a bracket for supporting the cell assembly. Provision is made for rotating the cell at a slow rate (30 rev/min) during a determination in order to minimize gravitational settling of coarser particles,

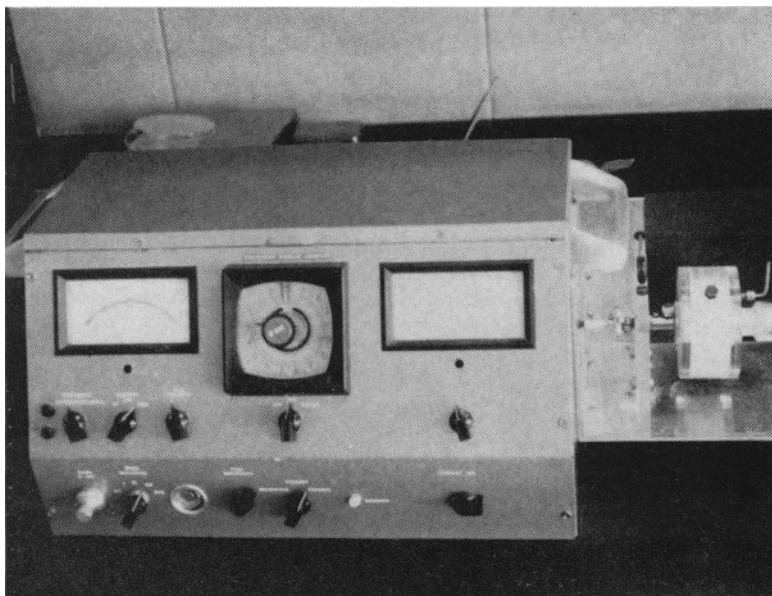


PLATE 1. The complete electrophoretic mass-transport apparatus. The cell is mounted at the right in a bracket that provides means for rotating the cell and supplying an electric current to the electrodes. The cabinet contains the constant-current power supply and timer.

and to dissipate thermal convections that would be created by the electric current passed through the suspension. For convenience, the instrument also contains an A.C. Wheatstone bridge resistance-measuring circuit operating at 1000 cps, which may be used with an external conductivity cell to determine the conductivity of the suspension being investigated; or alternatively, it may be used to measure the load resistance presented by the filled cell assembly.

Operating Procedure

The procedure for making a gravimetric determination of electrophoretic mobility is as follows. The component parts of the collection chamber are carefully cleaned and dried, and the electrode with its O-ring seal secured

to the chamber body by means of the threaded metal end cap. The chamber is filled with the suspension under study and weighed on an analytical balance. To aid in obtaining a reproducible volume of suspension, a close-fitting plug having a fine bore is temporarily inserted into the chamber entrance during each weighing. The collection chamber is then fitted to the reservoir, the reservoir filled to within about 10% of its capacity with remaining suspension, and the filling plug inserted to seal the reservoir. When dealing with coarse suspensions, there is a danger that sedimenting particles may enter the collection chamber from the reservoir during the time that the cell is vertically positioned for filling; to eliminate this source of error, the reservoir is provided with a movable shutter that closes the entrance to the collection chamber during the filling operation.

The filled cell assembly is mounted in the apparatus as shown in Plate 1. The cell is rotated by means of a motor coupled to the drive shaft extension on the filling plug and is supported at the other end by a spring-loaded pivot that engages a depression in the metal end cap; these same points are utilized to make electrical connection to the electrodes. Once the cell is rotating, the shutter can be swung clear of the collection chamber opening. A potential gradient is established between the electrodes upon passing a preselected current through the cell by means of the constant-current power supply; an automatic timer is used to control the duration of the run. At the end of the run, the cell is removed from its supports and the collection chamber detached, carefully wiped dry and reweighed. The increase (or decrease) in the mass of the collection chamber can now be used to calculate the electrophoretic mobility of the suspended particles.

Theory of the Mass-transport Cell

The electrophoretic mobility of particles is determined with the mass-transport cell by measuring the rate at which particles migrate into or out of the collection chamber. When the specific gravity of the particles is significantly different from that of the surrounding medium, the change in concentration of particles in the collection chamber is most readily determined gravimetrically. As this is a common circumstance, the following derivation assumes a gravimetric measurement; the necessary changes for other analytical techniques will be readily apparent.

The change in mass of the collection chamber is related as follows to the electrophoretic mobility of the particles.

- Let: v = velocity of the particles in cm sec^{-1} ,
 A = cross-sectional area of chamber entry in cm^2 ,
 M = concentration of solids in gcm^{-3} of suspension,

The mass of solids entering the chamber per second can be written:

$$W_1/t = vAM \quad (1)$$

As solids enter the chamber, they displace an equivalent volume of suspending liquid originally present; therefore, the mass of liquid leaving the cell per second can be written:

$$W_2/t = vAM\rho_w/\rho_s, \quad (2)$$

where ρ_s is the specific gravity of the particles and ρ_w is the specific gravity of the suspending fluid. The net change in the mass of the chamber is

$$\Delta W = W_1 - W_2.$$

So that

$$\Delta W/t = vAM(\rho_s - \rho_w)/\rho_s$$

or

$$v = \Delta W\rho_s/tAM(\rho_s - \rho_w). \quad (3)$$

The velocity of the solid particles, v , is the result of two components: the electrophoretic velocity of the particles into the chamber, and the velocity in the opposite direction of the liquid coming out of the chamber. Under conditions of steady flow we can write:

$$v = Ev_E - v_w,$$

where E is the potential gradient in volts cm^{-1} , v_E is the electrophoretic mobility in $\text{cm sec}^{-1}/\text{volt cm}^{-1}$ and v_w is the velocity of the liquid moving out of the chamber in cm sec^{-1} . Then:

$$v_E = (v + v_w)/E. \quad (4)$$

The velocity of the liquid, v_w , can be determined from the amount of liquid displaced, and the effective cross-sectional area of the cell entry:

$$v_w = vAM/\rho_s A(1 - M/\rho_s) \quad (5)$$

Substituting equations (5) and (3) into equation (4), and setting $M/\rho_s = \phi$, the volume fraction of dispersed phase, we obtain

$$v_E = \Delta W/tEA\phi(1 - \phi)(\rho_s - \rho_w). \quad (6)$$

The potential gradient, E , cannot be reliably determined from the overall applied potential because of polarization effects, and because of changes of cell resistance caused by the deposition of solids on the electrode of sign opposite to that of the particles. By maintaining a constant current through the cell, the effective voltage gradient at the entrance to the collection chamber can be computed from the current i , the area A , and the specific conductance λ :

$$E = i/\lambda A, \quad (7)$$

hence:

$$v_E = \Delta W\lambda/ti\phi(1 - \phi)(\rho_s - \rho_w). \quad (8)$$

Sources of Error

Equation (8) is used to compute electrophoretic mobility from experimental data. In its derivation, implicit assumptions were made that could affect its accuracy; these are:

1. The electrode contained in the collection chamber is reversible, i.e. no gases or other electrolysis products are formed that would significantly affect the volume of suspension contained.
2. The joule heat produced by the passage of electricity through the conducting suspension results in a negligible temperature rise in terms of system properties.

The first potential source of error is minimized by connecting the chamber electrode as the anode and using as an electrode material a metal above oxygen in the electromotive force series, such as zinc or lead, or by using an electrode reversible with respect to one of the ions present in the suspension, such as Ag/AgCl in the case of chloride ion. Both types of electrode systems have been used successfully.

The second source of error, that due to heating, can be serious unless certain precautions are observed, as can be shown by calculation. The joule heat, P , is given by

$$P = i^2 R,$$

hence the greatest temperature rise will occur at the point of highest resistance, namely, the entrance to the collection chamber. Using equation (7), the expression for joule heat within the entrance tube becomes

$$P = E^2 \lambda A \text{ watts cm}^{-3}$$

where E , as before, is the effective voltage gradient. For the cell used in this work, $A = 0.317 \text{ cm}^2$; taking the specific heat of the suspension as equal to 1, we obtain

$$P = 0.076 E^2 \lambda \text{ cal. sec}^{-1} \text{ cm}^{-3}$$

or

$$\Delta T = 0.076 E^2 \lambda ^\circ\text{C sec}^{-1}.$$

A typical value for E would be 20 volts cm^{-1} ; taking the conductivity of a dilute electrolyte solution as of the order of $1 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ gives

$$\Delta T = 0.003^\circ\text{C sec}^{-1}.$$

Since 300 sec is ordinarily adequate time for a determination, the maximum temperature rise, assuming no heat loss, would be of the order of 1°C . If, however, more concentrated electrolytes are used, such that $\lambda = 1 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, calculation would indicate a maximum possible temperature rise of 100°C ; in actuality, the rise would be much less. Assuming that all the heat loss occurs by conduction through the suspension to the ends of the entrance tube, it can be shown that at equilibrium the maximum temperature rise above the end temperature would be

$$\Delta T = P l^2 / 2k$$

where l is the half-length of the tube and k is the thermal conductivity of the liquid. Applying this expression to the case where $\lambda = 1 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, and $l = 0.5 \text{ cm}$, we now find a ΔT of approximately 2.5°C , rather than 100°C .

The significance of a temperature change of this magnitude can be estimated as follows. The electrophoretic velocity of the suspended particles is related to their zeta potential by the approximate expression

$$v = D\zeta i / 4\pi\eta\lambda A$$

when D is the dielectric constant and η the viscosity of the suspending liquid. Assuming that ζ is independent of temperature over the narrow range considered, then the temperature coefficient of v will be the same as that for the term $D/\eta\lambda$. But the product $\eta\lambda$ is very nearly a constant, a generalization referred to as Walden's Rule; the relative variation of v with temperature will therefore be very nearly the same as that of the dielectric constant: i.e. -0.5% per $^\circ\text{C}$, near room temperature. It may be necessary, therefore, when working with highly conducting suspensions, to employ a reduced voltage gradient to minimize this effect; alternatively, by maintaining a constant value of P in a series of measurements involving a wide range of conductivities, the temperature rise can be held constant.

EXPERIMENTAL RESULTS

The data presented in this paper are intended primarily to illustrate the use of the mass-transport cell and to show some of the interrelations that exist between electrophoretic mobility and bulk system properties; these will be explored in greater detail in future publications.

The kaolin sample used in the present work was prepared from clay obtained from the Freeport Kaolin Company mines near Gordon, Ga. The crude kaolin was blunged with water at approximately 30% solids by weight and deflocculated by the addition of NaOH to a pH of 9. The kaolin slip was allowed to undergo sedimentation to remove particles larger than about 10 microns. The fine fraction so obtained was decanted and then flocculated by the addition of H_2SO_4 to bring the pH to about 4.5 and stored in plastic containers.

For use in this work, a quantity of the purified kaolin sufficient for all measurements was treated with an excess of mixed cation and anion exchange resins in their hydrogen and hydroxyl forms respectively. In this way, a suspension having a very low ionic strength was obtained without subjecting the kaolin to either strongly acid or alkaline conditions. The deionizing process was followed conductimetrically; the initial stock slip had a specific conductance of $2.55 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$; the treated slip, following removal of the exchange resins by screening, had a specific conductance of $1.0 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$, which would indicate an electrolyte concentration well below 10^{-5} N . Some physical and chemical properties of the deionized kaolin are given in Table 1.

TABLE 1.—PHYSICAL AND CHEMICAL CHARACTERISTICS OF KAOLIN SAMPLE

Particle size by sedimentation	Impurity analysis*	I.C.I. color
100%—20 microns	0.01% P ₂ O ₅	Dominant wavelength 5780 Å
91%—10 microns	0.02% SO ₃	Visual efficiency 89.7%
85%—5 microns	0.052% K ₂ O	Excitation purity 4.9%
78%—2 microns	0.015% CaO	
53%—1 microns	1.36% TiO ₂	
	0.257% Fe ₂ O ₃	

* X-ray diffraction shows the sample to be well crystallized with no impurities detectable except anatase.

The deionized suspension, and portions of the suspension containing increasing amounts of tetrasodium pyrophosphate (TSPP), were adjusted to 20% solids by weight and the electrophoretic mobility of the particles determined in duplicate with the mass-transport cell. The pH of the centrifugates, specific conductance, NaCl flocculation value, and rheological properties of the suspensions were also determined; these data are reported in Table 2 together with the measured weight gain of the collection chamber and operating conditions for the mobility determinations.

The reproducibility of filling and weighing the collection chamber was found to be about ± 0.002 g. The mean deviation of repeated mobility determinations averaged about $\pm 0.02 \times 10^{-4}$ cm sec⁻¹/V cm⁻¹.

The flocculation values reported are in terms of the concentration of NaCl, in meq per liter, required to produce a just-visible clear supernatant layer on the suspension 2 hr after the addition; these values were determined on 20% solids suspensions.

Rheological properties of the suspensions were determined using a Ferranti-Shirley cone-plate viscometer fitted with a 3.5 cm radius cone having a cone angle of 20'35". This allowed flow curves to be determined at shear rates up to 17,400 sec⁻¹; the sample temperature was maintained at 25.0 \pm 0.1°C. Typical flow curves at several TSPP levels are reported in Fig. 2; these curves are characterized in Table 2 by the value of the apparent yield point obtained by extrapolation of the linear high shear portion of the rheograms, and by the viscosity corresponding to the slope of this same linear region.

DISCUSSION

A graphical correlation of the measured properties of the suspensions as a function of percent TSPP by weight of kaolin is shown in Fig. 3. It will be noted that while the electrophoretic mobility of the particles increases rapidly with the first small additions of TSPP, the system remains flocculated until about 0.10% TSPP has been added. This is illustrated more clearly in Figs. 4a, b. Figure 4a shows that the apparent yield point becomes zero at a

TABLE 2.—EXPERIMENTAL RESULTS

$\text{Na}_4\text{P}_2\text{O}_7$ (%)	F^*	λ (ohm $^{-1}$ cm $^{-1} \times 10^6$)	i (ma.)	W (grams)	Time (sec)	pH	Differential viscosity (cp.)	Yield point (dyne cm $^{-2}$)	v_E^\dagger
0.00	0	0.989	0.070	0.0981	120	6.2	3.01	189	0.905
		1.00	0.075	0.1983	240				0.855
0.02	0	6.30	0.450	0.3693	180	6.25	2.80	100	2.24
		6.24	0.460	0.3778	180				2.25
0.04	0	12.0	0.55	0.2947	180	6.5	2.56	34	2.78
		10.8	0.53	0.3060	180				2.72
0.06	0	23.1	0.87	0.4044	300	6.5	2.26	13	2.79
		23.1	0.87	0.2604	180				3.00
0.10	3	54.8	1.38	0.3042	300	6.2	2.13	0	3.14
		53.4	1.39	0.3069	300				3.15
0.15	22½	128.0	2.03	0.3009	450	6.7	2.03	0	3.33
		127.0	2.02	0.3046	450				3.39
0.20	65	256.0	2.90	0.2481	450	6.70	2.00	0	3.83
		259.0	2.90	0.2467	450				3.86
0.30	70	510.0	4.10	0.2626	600	7.90	1.91	0	4.32
		513.0	4.10	0.2616	600				4.30
0.40	—	729.0	4.81	0.2329	600	8.4	1.93	0	4.64
		755.0	4.82	0.2238	600				4.56

* Flocculation value, meq NaCl/l.

† Mobility, cm sec $^{-1}$ /V cm $^{-1} \times 10^{-4}$.

mobility of about $3.25 \text{ cm sec}^{-1}/V \text{ cm}^{-1}$, indicating a deflocculated system. The data of Fig. 4b illustrate the same point in terms of the apparent and differential viscosities.

At TSPP levels above 0.1% the pH and specific conductance begin to increase more rapidly; at this same point, the stability of the suspension toward added electrolyte increases abruptly, as shown in Fig. 3.

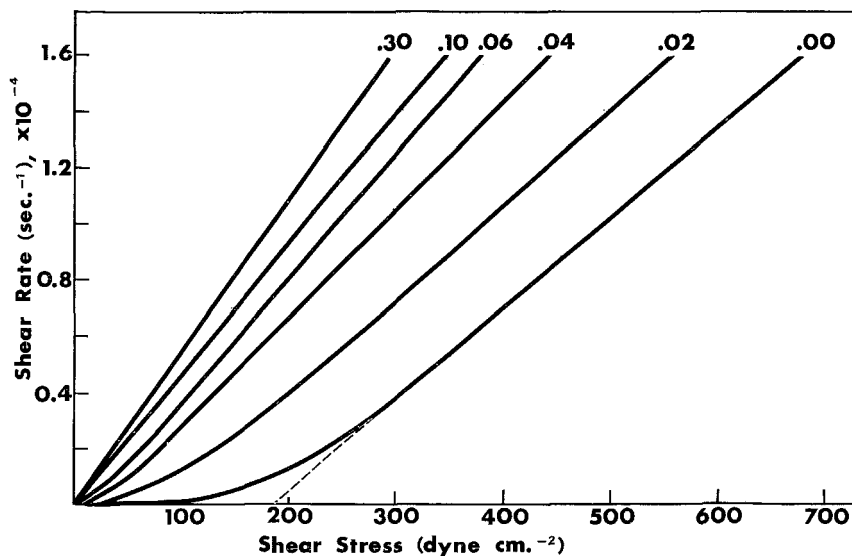


FIG. 2. Rheograms of 20 wt% deionized kaolin slurries at several levels of tetrasodium pyrophosphate addition; the figures on the curves indicate % TSPP by wt of clay. An extrapolation of the linear region was used to determine an apparent yield point; the slope of this line was used to calculate the differential viscosity.

The present data can be qualitatively interpreted in terms of the accepted view that, in the absence of strongly adsorbed anions, the edge surfaces of kaolinite plates carry a positive charge, while the crystal faces are negatively charged. This leads to strong edge-to-face attractive forces and a flocculated system. Lyons (1964) has shown that the edge surfaces of kaolinite have an adsorptive capacity for about 0.05% tri(poly)phosphate ion; the rapid increase in particle mobility at TSPP additions up to about 0.05% is interpreted, therefore, as being due to the specific adsorption of pyrophosphate ion on the kaolinite edges. The increase in mobility at higher phosphate levels is attributed to a weaker generalized adsorption of phosphate and to the effect of increased hydroxyl ion concentration.

The fact that stability toward electrolytes and complete deflocculation of the system does not occur until the pyrophosphate level exceeds 0.10% is

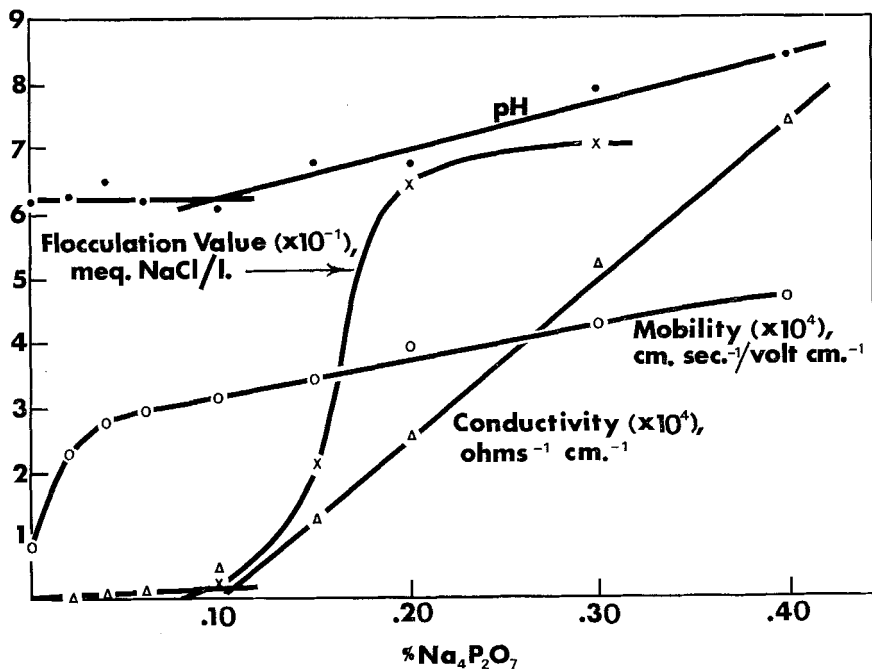


FIG. 3. A graphical correlation of the data reported in Table 2 with wt% TSPSP added.

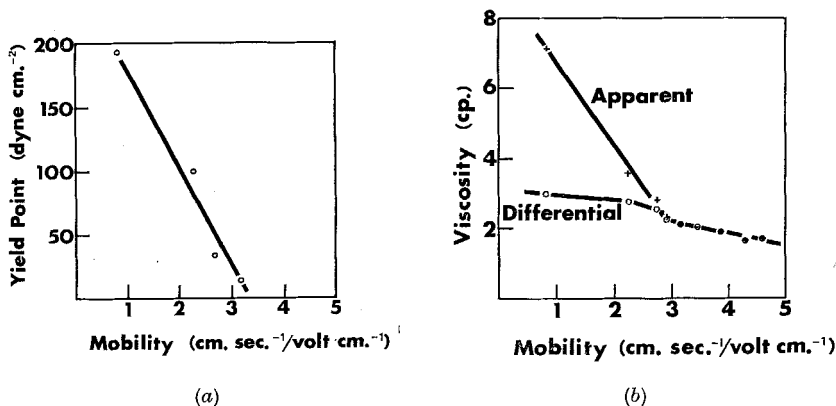


FIG. 4. (a) The variation of apparent yield point of 20 wt% solids suspensions with measured electrophoretic mobility. Complete deflocculation is seen to occur at 3.25×10^{-4} cm sec.⁻¹/V cm.⁻¹. (b) The variation of apparent viscosity at 8700 sec.⁻¹ and differential viscosity (at high shear rate) with electrophoretic mobility.

accounted for in terms of the theory of Verwey and Overbeek (1948). Even though the positive edge charge of the kaolinite crystals may be neutralized at *ca.* 0.05% TSPP, a negative potential sufficient to create effective repulsive forces is not developed until higher phosphate and hydroxyl ion concentrations are reached.

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