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AN INTERPRETATION OF THE SEDIMENTATION BEHAVIOR OF PHARMACEUTICAL KAOLIN AND OTHER KAOLIN PREPARATIONS IN AQUEOUS ENVIRONMENTS

K. S. Alexander, J. Azizi, D. Dollimore and F. A. Patel, College of Pharmacy and Department of Chemistry, The University of Toledo, Toledo, Ohio 43606

ABSTRACT

The effect of flocculant materials on kaolin-water suspensions is reported using two kaolins. One of these is a pharmaceutical-grade kaolin and the other an industrial kaolin. These two systems serve as a model in a broader investigation which will systematically study the ancillary ingredients of pharmaceutical kaolin-based suspensions. These studies are based on concentrated suspensions where fall of particles is hindered and characterized by sedimentation "en bloc" with a sludge line serving as interface between the supernatent liquid and the settling suspension. It is shown that there is an optimum concentration of macromolecular flocculant which causes maximum flocculation. At higher concentrations of flocculant the system is stabilized. Two approaches are used to explain the results. The first represents the phenomenon as a modification of Stokes Law results. A correlation is found between the parameter A used as a characterization constant in Steinour's empirical relationship and the Richardson and Zaki exponent *n*. A theoretical justification of this relationship is provided. A permeability relationship is used in the second approach based on the application of permeability equations put forward by Kozeny-Carmen. The variable *k* in the resultant equation is shown in theory and in practice to have a minimum at some value of porosity determined by the nature of the concentrated suspension. This treatment is applied here to flocculated systems. The systems are found in general to show very high hindrance.

INTRODUCTION.

In this study the effect of flocculant materials on kaolin-water systems is reported using two kaolin systems. One of these systems utilizes a pharmaceutical grade product and the other an industrial kaolin. These two systems serve as models in a broader investigation.[1,2] This wider investigation has included a systematic study of ancillary ingredients of pharmaceutical suspensions. Many pharmaceutical formulations are produced in the form of concentrated suspensions. In a previous publication [1], calcium carbonate suspensions were used as a "model" for the behavior of such suspensions. This system settled appreciably without the use of additives. In the present case, the suspension of kaolin in water was very stable, but flocculation was easily induced by the addition of flocculants.

The behavior of concentrated suspensions of powders in a liquid medium cannot be treated by the direct application of the normal principles of free fall. The behavior of a single particle falling in an infinite volume of fluid follows from a consideration of Stokes Law. However, above a certain concentration, the fall of any particular particle is "hindered" by the presence of others. In this hindered settling region, the suspension settles "en bloc" with a well-marked upper boundary. On one side of this boundary is a relatively clear supernatent liquid below the boundary is the settling suspension. Theoretical and empirical relationships allow the average particle (or floc) radius in suspension to be calculated from observations of the rate of fall of the interface. In dilute suspensions, the behavior can clearly be seen to be obeying Stokes Law. As the suspension concentration increases, the system is seen to change and the hindered settling region is observed where the interface occurs between the settling suspension and clear supernatant liquid. The derived relationships, as already noted, are all based on the observation of the rate of fall of the interface. Two interpretations are found in the literature [2]. One set of theories regard the problem as initially a modification which must be applied to the classic equations for dilute suspensions based on Stokes Law. The second approach is based on the idea that the settling behavior can be explained in terms of permeability [3]. The Kozeny-Carmen equation is utilized and the settling behavior is explained on the basis of water permeating out of the suspension [4-7].

A distinction must be drawn between coagulation of particles and the term flocculation applied to the kaolin-water suspensions investigated in the present study. The term coagulation is used here to represent aggregation by charge neutralization brought about by the addition of multivalent ions to the system. The addition of certain neutral polymers to the kaolin-water system at an optimum concentration may cause flocculation. This term is usually reserved for a polymer bridging mechanism where the aggregation is brought about by the adsorption of the polymer at various surface sites on the kaolin belonging to more than one kaolin particle. An increase in flocculant ability is often caused by using polymers carrying an ionic charge. Various polymeric flocculants may be used for this purpose. Since the intention of this study was to establish a model system capable of extensive analysis, the flocculants used in this initial study on kaolin differ from the ingredients used in commercial pharmaceutical suspensions. The flocculants used here were commercial polymer flocculants. It is essential to realize that the addition of extra ingredients modifies the behavior of the suspension. The simple flocculant model system described in the present study and in the previous publication[1] have been expanded step by step and will be reported in future publications.

EXPERIMENTAL METHOD

In the experiments described here, the rate of fall of the interface or the "sludge" line in the concentrated suspensions is an obvious property which can easily be followed. The kaolins used here were of two types, Kaolin NF, a pharmaceutical grade kaolin, and an industrial kaolin. Kaolin is a hydrated aluminum silicate. Properly speaking, the term, kaolin, is the name of a group of minerals which includes kaolinite, dickite, nacrite, and halloyrite. However, in the pharmacy industry the term, kaolin, is used instead of kaolinite and that practice will be continued in this paper. The ideal formula for the kaolin group is $Al_2 Si_2 O_5 (OH)_4$. However, the aluminium can be partially replaced by iron or magnesium or with an exchangeable ion, such as calcium, to make up an overall charge deficiency. Worrel[8] represents a typical formula as $(Al_{1.8} Fe_{0.1} Mg_{0.1}) Si_{2.0} O_{5.0} (OH)_{4.0} \rightarrow Ca_{0.05}$. Kaolin NF is a light kaolin free from gritty particles and not containing a dispersing agent. Electron microscopy confirmed the hexagonal nature of the clay crystals. The industrial kaolin was a Georgia kaolinite. The percentage composition of the Georgia Kaolin was $Si O_2$, 45.1 (theor 46.2); $Al_2 O_3$, 37.7 (theor 39.8); H_2O, 13.4, (theor 13.9); with trace elements determined as Fe_2O_3, 0.10%; MgO, 0.14%; TiO_2, 0.040%; CaO, 0.30%; CuO, 0.005%; Na_2O, 0.10%; and K_2O, 0.0077%. The corresponding trace element content of the Kaolin NF was Fe_2O_3, 0.094%; MgO, 0.012%; TiO_2, 0.029%, CaO, 0.040%; CuO, 0.006%: Na_2O, 0.20%; and K_2O, 0.005%. Various polymeric flocculants and additives were used in this study. This includes tragacanth (in ribbon and powder form) which is the dried gummy exudate from Astragalas gummifier. Further details of this material as a flocculant has been given in previous publications[9]. Pectin is the purified carbohydrate product obtained from the dilute acid extract of the inner portion of the rind of citrus fruits or from apple pomace. Carboxymethylcellose (CMC) is recommended and used as a stabilizing agent for many suspensions. Polyvinylpryollidone is also used as a dispersing and suspending agent in certain suspensions. Various grades (as specified) of polyacrylamide flocculating agents were also tested on the Georgia kaolin suspensions.

The hindered settling experiments involve the use of measuring cylinders of approximately 250 ml capacity. The total volume of the suspension used throughout the experiments was 150 ml. A ruler placed alongside the cylinder enabled the position of the "sludge line" at any time to be ascertained. The suspension was prepared by adding a known amount of the clay to the cylinder and then 75 ml of distilled water alone or containing whatever polymer flocculant required was added. The suspension was then shaken, made up to 100 ml and then allowed to stand overnight. It was shaken again the next day and made up to 150 ml before performing the experiment. The system was redispersed prior to the hindered settling experiment by inverting the cylinder up and down for 25-30 times (approximately 50-60 sec).

The experiment involved measuring the position of the interface against time. The suspension was left overnight and the final settled volume was also noted. The clarity of the suspension was also noted using a technique which has been described elsewhere[10]. All the systems were subjected to rate of fall observation, but the final settled volume and clarity of the supernatent was only reported on selected systems.

The mode of settling may be affected by numerous factors. The affect of varying amounts of clay in the system and the presence of small amounts of flocculant material have been investigated in this study.

DISCUSSION AND RESULTS

A typical hindered settling experiment is shown schematically in Figure 1. In this type of experiment the amount of kaolin present in the suspension was altered. It is the nature of these tests which allows the theories of hindered settling to be developed. The assessment of the various flocculating agents was made by fixing the amount of kaolin at 15 g and varying the amount of flocculant present. The rate of fall of the interface (Q) was measured from the middle linear portion of the plots shown in Figure 1.

The general observation regarding the effect of polymer flocculants and additives agreed with previous reports in that for a given quantity of kaolin (15 g), the polymer flocculants had an optimum effect on flocculation at a relatively low concentration. Beyond this value of polymer concentration, the suspension was in fact stabilized. Figure 2 shows the effect of gum tragacanth on kaolin NF and Figure 3, the effect on Georgia kaolin. Table 1 lists the optimum concentration of various polymers necessary to achieve maximum flocculation for the kaolin NF clays as determined by noting the maximum rate of settling of the interface Q. Similar data for the Georgia

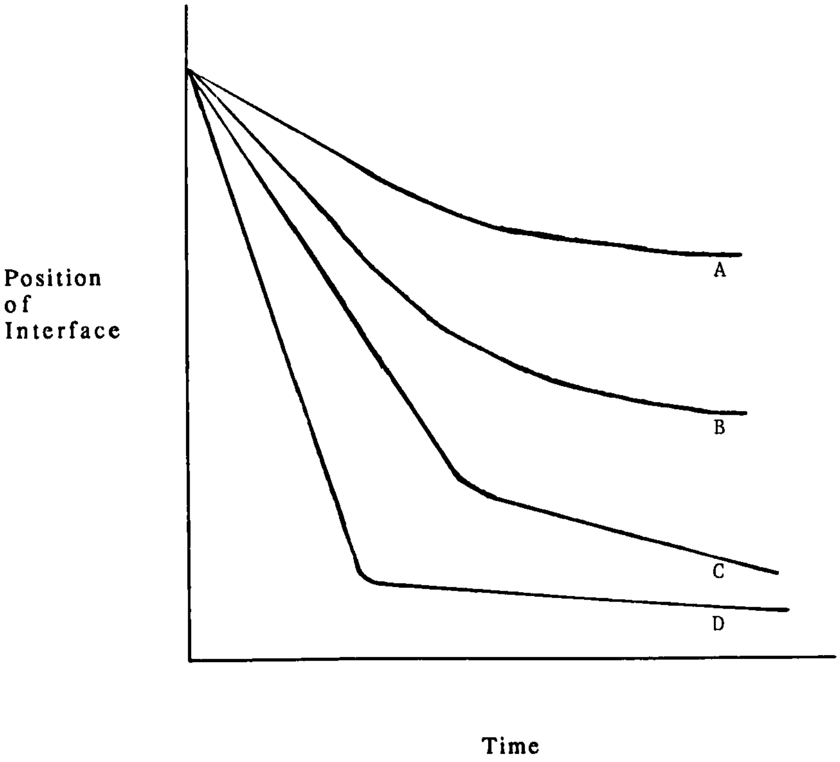

Figure 1: Schematic portrayal of the rate of fall of the interface for kaolin systems. Amount of material increases from A to D.

kaolin is given in Table 2. The optimum values for the final settled volume and the clarity of the supernatant are given in Tables 3 and 4. It will be observed that they did not necessarily coincide with the optimum concentration of flocculant needed for maximum flocculation. In the case of the hydrocolloids, macromolecules which with increasing concentration give a large increase in viscosity, there was generally a continued increase in the final settled volume up to a constant value with increasing amounts of added polymer. A non-coincidence of maximum conditions of polymer concentration for clarity, final settled volume, and settling rate (Q) for polyacrylamide flocculants has been reported previously[11].

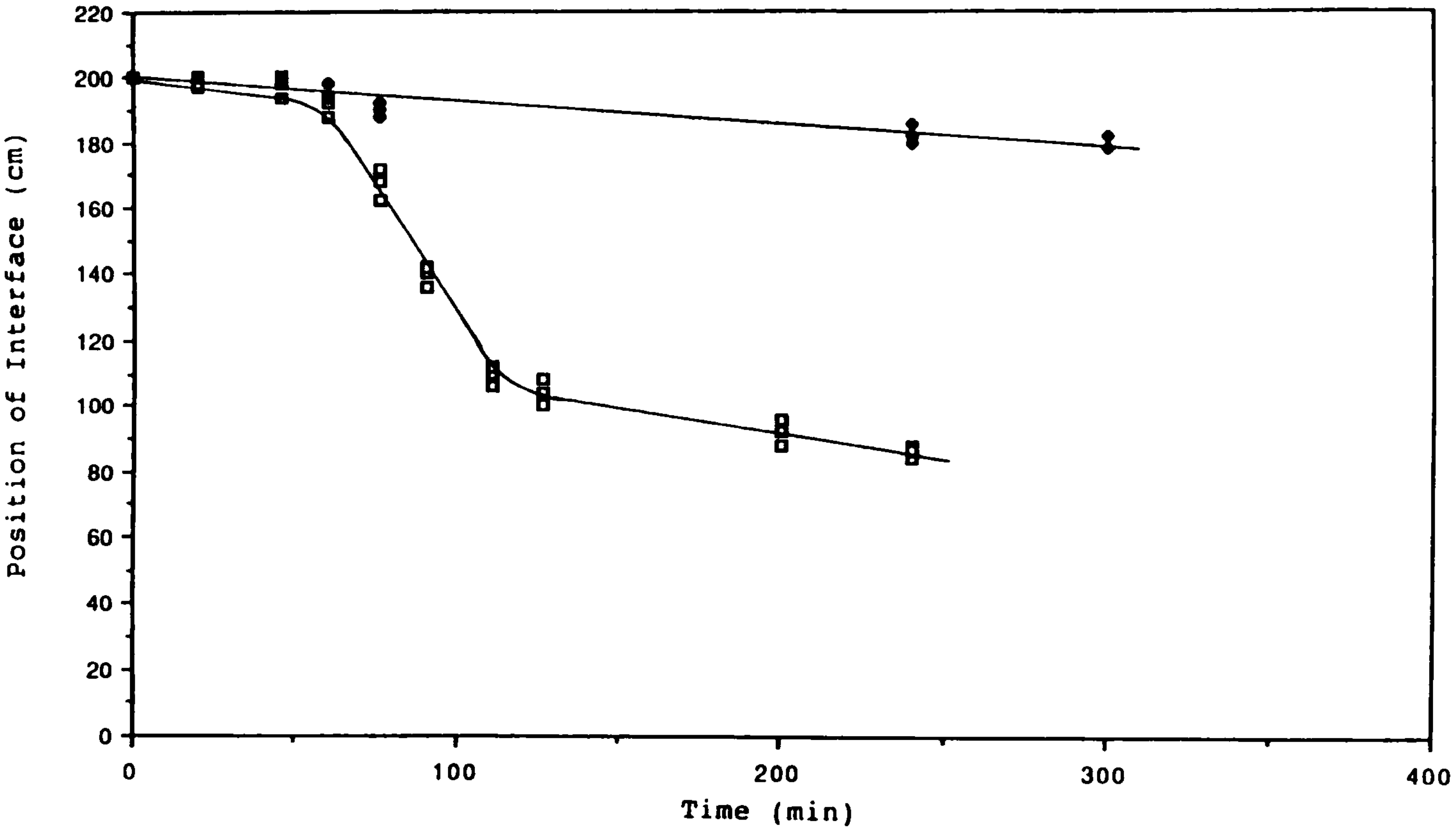

Figure 2: Settling behavior of 15 g of Kaolin NF in the presence of tragacanth (powder grade) at concentration of 2500 ppm (□) and 3000 ppm (•).

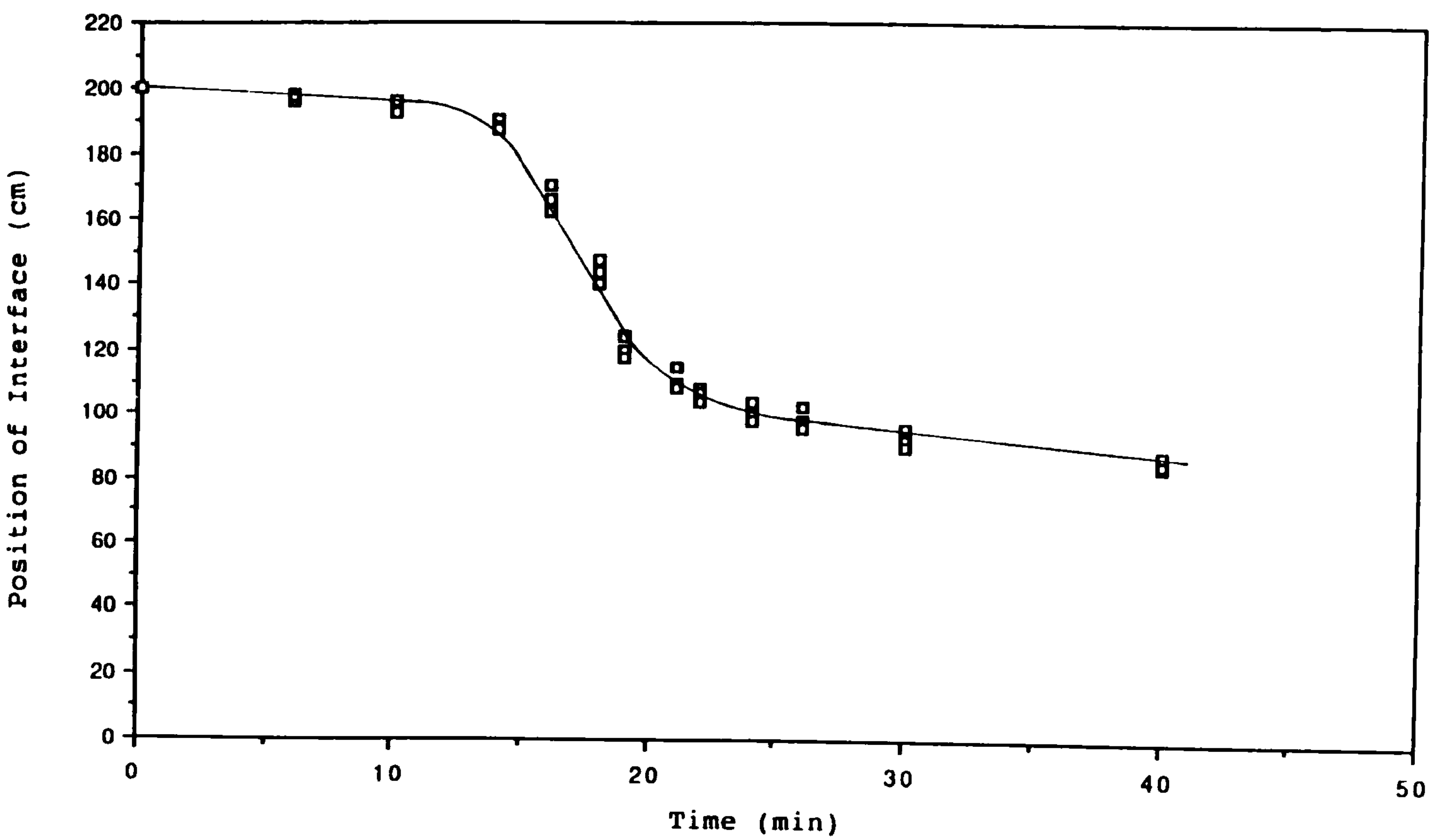

Figure 3: Settling behavior of 15 g of Georgia Kaolin in the presence of tragacanth (ribbon grade) at a concentration of 2000 ppm.

Table 1

The Optimum Concentration of Flocculant Needed to Achieve Maximum Rate of Settling of the Clay-Kaolin NF

Polymer	Optimum Concentration ppm
Tragacanth (ribbon grade)	1600
Tragacanth (powder grade)	2500
Polyvinylpyrollidone	300 - 400
Carboxymethylcellulose	Stablized the suspension at all concentrations
Pectin	Stablized the suspension at all concentrations

Experiments performed on 15 g of kaolin in a total of 150 ml of suspension.

Table 2

The Optimum Concentration for Flocculant Needed to Achieve Maximum Rate of Settling for the Georgia Kaolin

Polymer	Optimum Concentration pp
Tragacanth (Ribbon Grade)	700
Tragacanth (Powder Grade)	2000
Polyvinylpyrollidone	100 - 400
Carboxymethylcellulose	Stabilized the suspension at all concentrations
Pectin	Stablized the suspension at all concentrations
Agefloc WT-40	80 - 200
Agefloc WT-20	20 - 200
Agefloc A-50	100
Floxan SC-5080	120 - 270
Secofloc 450	15 - 40
Secofloc 601	15 - 120

Notes
1) The experiments with Tragacanth, Polyvinylpyrollidone, carboxymethylcellulose, and pectin were carried out on a suspension of total volume, 150 ml.
2) The experiments on commercial flocculants, Ageflocs, Floxan and Secofloc (with various designated numbers) were carried out on 20 g of clay in a total suspension of 150 ml.
3) The active flocculating ingredient of the ageflocs was poly (dimethyl diallyl) ammonium chloride.
4) Floxan and Secofloc were all modified polyacrylamides

Table 3

Optimum Concentrations of Polymer Needed to Give Maximum Final Settled Volume and Maximum Clarity of the Supernatant for the Clay-Kaolin NF.

Polymer	Optimum concentration settled volume/ppm	Optimum concentration supernatent/ppm
Tragacanth (ribbon grade)	1600	1600
Tragacanth (powder grade)	2500	3000
Polyvinyprollidone	400	400
Carboxymethyl-cellulose	50	No optimum observed
Pectin	800 and still increasing	800 and still increasing

Experimental conditions were identical to those given in Table 1.

Table 4

Optimum Concentrations of Polymer Needed to Give a Maximum Final Settled Volume and Maximum Clarity of the Supernatent for the Georgia Kaolin.

Polymer	Optimum concentration for final settled volume/ppm	Optimum concentration for maximum clarity of supernatent/ppm
Tragacanth (ribbon grade)	1600 and increasing	800
Tragacanth (powder grade)	3500 and increasing	3500 and increasing
Polyviny-pyrollidone	100-400	200
Carboxymethyl-cellulose	Constant value recorded at all concentrations	100
Pectin	Constant value recorded at all concentrations	Constant value recorded at all concentrations
Agefloc WT-40	120	120
Agefloc WT-20	450 and increasing	200
Agefloc A-50	270	200
Floxan SC-5080	130	80
Secofloc 450	Constant value recorded at all concentrations	90
Secofloc 601	105	130

Table 5

Variation of the Rate of Fall of the Interface (Q) with the Amount of Georgia Kaolin. Flocculant Used was Agefloc A-50 at a Concentration of 75.0 ppm.

Mass of Clay g	Rate of Fall cm sec^{-1} Q	Initial Porosity ε	$Q(1-\varepsilon)$
5.00	0.026	0.986	3.55×10^{-4}
7.00	0.025	0.981	4.86×10^{-4}
10.00	0.022	0.973	6.04×10^{-4}
15.00	0.021	0.959	8.65×10^{-4}
20.00	0.012	0.046	6.64×10^{-4}

The experimental plots, where the amount of kaolin was varied, can be plotted as Q against the initial porosity of the system (ε). Here, and in subsequent treatments, ε represents the liquid volume fraction of the uniformly mixed suspension at the start of each hindered settling experiment. A typical series of experiments for the Georgia kaolin with Agefloc A-50 and with Floxan EA4443 is given in Tables 5 and 6. It will be observed that as the mass of clay increases in each experiment so the rate of fall of the interface decreases. This is also true for the studies with Kaolin NF. Figure 4 shows the experimental data for the kaolin-polyvinylpyvollidone system which demonstrates the point very well.

Before continuing with the development of the theory, one other direct experimental observation may be made. The term, solid flux, $Q(1-\varepsilon)\,\rho_s$, where ρ_s is the density of the solid, represents the mass transfer of solid per unit cross section area per unit time down the sedimentation column. It is a measure of solid transport. It has been established[12] that a complete system goes through a maximum as the initial porosity is increased. This is seen to be the case for the data in Table 6, but all the data portrayed in Table 5 lies beyond this maxima.

The Modified Stokes Law Approach

One method of approaching the problem of hindered settling is to modify the equation for a single particle resulting from the application

Table 6

Variation of the Rate of Fall of the Interface (Q) with the Amount of Georgia Kaolin. Flocculant Used was Floxan EA 4443 at a concentration of 75.0 ppm.

Mass of Clay g	Rate of Fall cm sec^{-1} Q	Initial Porosity ε	Q (1 - ε)
3.00	0.68	0.991	5.51×10^{-3}
5.00	0.61	0.986	8.30×10^{-3}
10.00	0.56	0.973	15.32×10^{-3}
12.50	0.41	0.966	13.95×10^{-3}
15.00	0.30	0.959	12.16×10^{-3}
17.50	0.21	0.952	10.19×10^{-3}
20.00	0.15	0.046	8.16×10^{-3}

of Stokes Law. The law applied to a single spherical particle falling at a uniform velocity V_s under gravity has the relationship

$$V_s = \frac{2gr^2 (\rho_s - \rho_s)}{9n} \qquad \text{Eq.1}$$

where r is the radius of the particle, g is the acceleration due to gravity, ρ_s is the density of the fluid and η is the coefficient of viscosity.

Steinour[13] modified this equation by the introduction of a single function $\phi(\varepsilon)$ to account for hindered fall and a term for the porosity (ε).

$$Q = \frac{2g^2 (\rho_s \, \rho_p) \, \varepsilon^2 \, \phi(\varepsilon)}{9n} \qquad \text{Eq. 2}$$

Steinour derived an explanation for $\phi(\varepsilon)$ from the considerations of the hydraulic radius of the suspension; which he gave as:

$$\phi(\varepsilon) = \frac{\varepsilon}{1 - \varepsilon} \, \theta(\varepsilon) \qquad \text{Eq. 3}$$

where $\theta(\varepsilon)$ represents those effects of shape that are not evaluated by

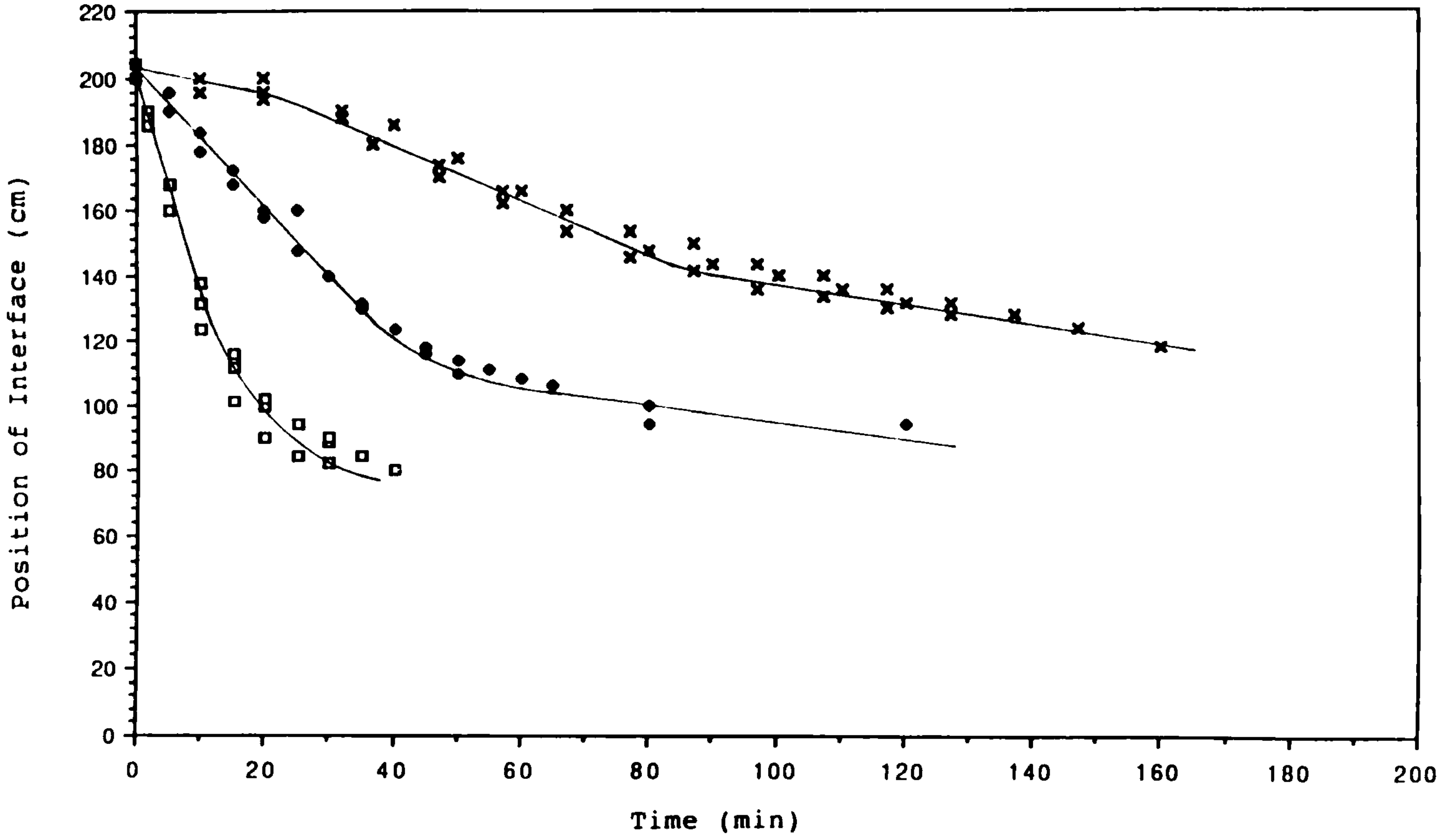

Figure 4: Settling behavior of Kaolin NF - Polyvinylpyrollidone system (350 ppm).

using the hydraulic radius. Steinour's final equation then takes the form:

$$Q = \frac{V_s \varepsilon^3 \theta(\varepsilon)}{(1 - \varepsilon)} \qquad \text{Eq. 4}$$

Equation 4 can be rearranged and modified to give

$$\{Q(1 - \varepsilon)\}^{1/3} = \{V_s \theta(\varepsilon)\}^{1/3} \varepsilon \qquad \text{Eq. 5}$$

and plots of $\{Q\ (1\text{-}e)\}^{1/3}$ against ε should be linear if $\{V_s\ \theta(\varepsilon)\}^{1/3}$ was constant. For this to be so, it depends very much on the form of $\theta(\varepsilon)$. However there are linear plots of this type in the literature which upon greater detailed analysis often shows a "kinked" relationship of two linear regions[14].

Other relationships have been suggested by Steinour. An empirical relationship which he used takes the form

$$Q = V_s \varepsilon^2 10^{-A(1-\varepsilon)} \qquad \text{Eq. 6}$$

where A is a constant for each experimental system and can be calculated from plots of log (Q/ε^2) against (ε). Plots of such data for the Georgia kaolin with tragacanth (ribbon grade) and polyvinylpyrollidone suspensions are shown in Figures 5a and 5b. Typical values of A calculated in this way are given in Table 7. It is seen that A varies from system to system.

Comparing coefficients in equations (3) and (6) gives:

$$\theta(\varepsilon) = \left(\frac{(1 - \varepsilon)}{\varepsilon} \right) 10^{-A(1-\varepsilon)} \qquad \text{Eq. 7}$$

Plots of $\theta(\varepsilon)$ against ε for Kaolin NF - Tragacanth system where (A = 21.39) and the Kaolin NF - polyvinylpyrollidone system where A = 53.42 are shown in Figure 6. The variation of $\theta(\varepsilon)$ with ε is complex and unique to each system and calculated value of A. It is easier to characterize the system by noting the single value of A. Additionally, Richardson and Zaki[15] gave the relationship between Q and ε as:

$$Q = V_s \varepsilon^n \qquad \text{Eq. 8}$$

FIGURE 5-a

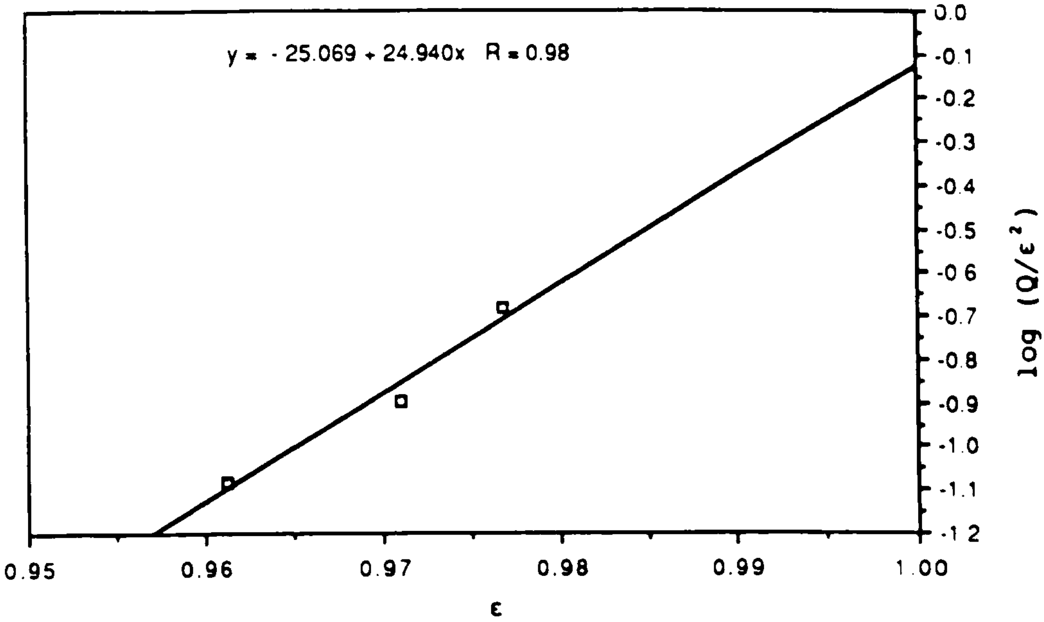

FIGURE 5-b

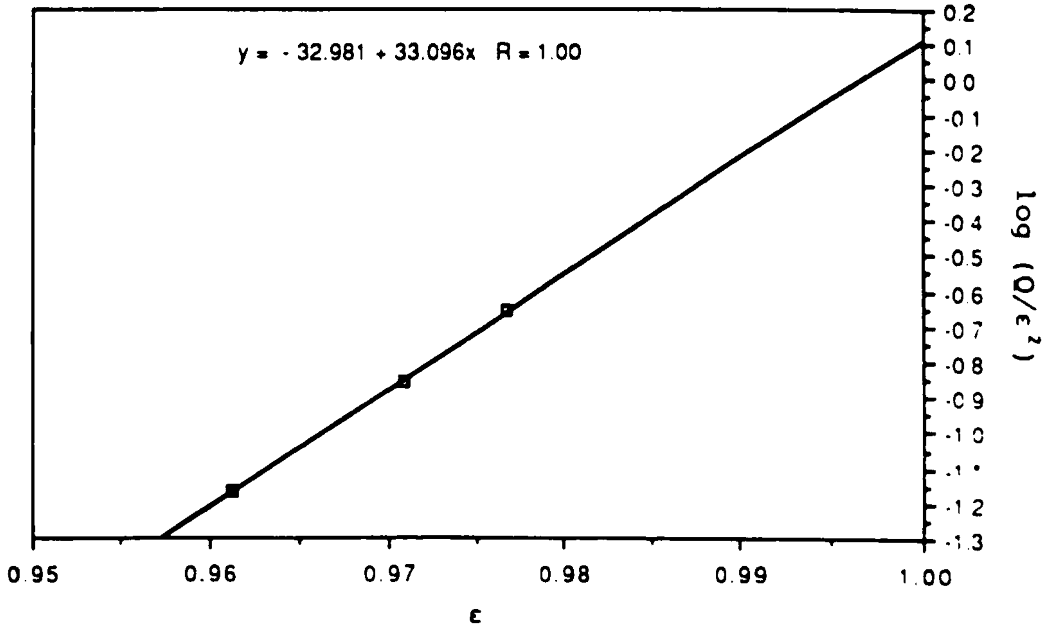

Figure 5: Plots of log (Q/ε^2) versus ε for Georgia Kaolin with: a) ribbon type tragacanth 700 ppm; b) polyvinylpyrollidone 300 ppm.

Table 7

Values of the Parameter A (see Eq. 6) for the Kaolin Systems and the *n* Value Obtained from the Richardson and Zaki Equation (Eq. 8).

Suspended Material	Flocculant	A	*n*	*n*/A
Kaolin NF	Tragacanth	21.39	21.39	2.24
	Polyvinylpyrollidone	53.42	122.16	2.29
Georgia Kaolin	Tragacanth	24.94	58.01	2.33
	Polyvinylpyrollidone	33.09	59.09	1.79
	Secofloc 650	12.19	26.03	2.14
	Secofloc 611	7.25	14.63	2.02
	Floxan EA4443	11.59	24.64	2.13
	Floxan SC-5010	14.46	31.26	2.16
	Floxan SC-5080	13.61	29.30	2.15
	Agefloc WT-40	29.39	65.67	2.23
	Agefloc A-50	11.05	23.39	2.12

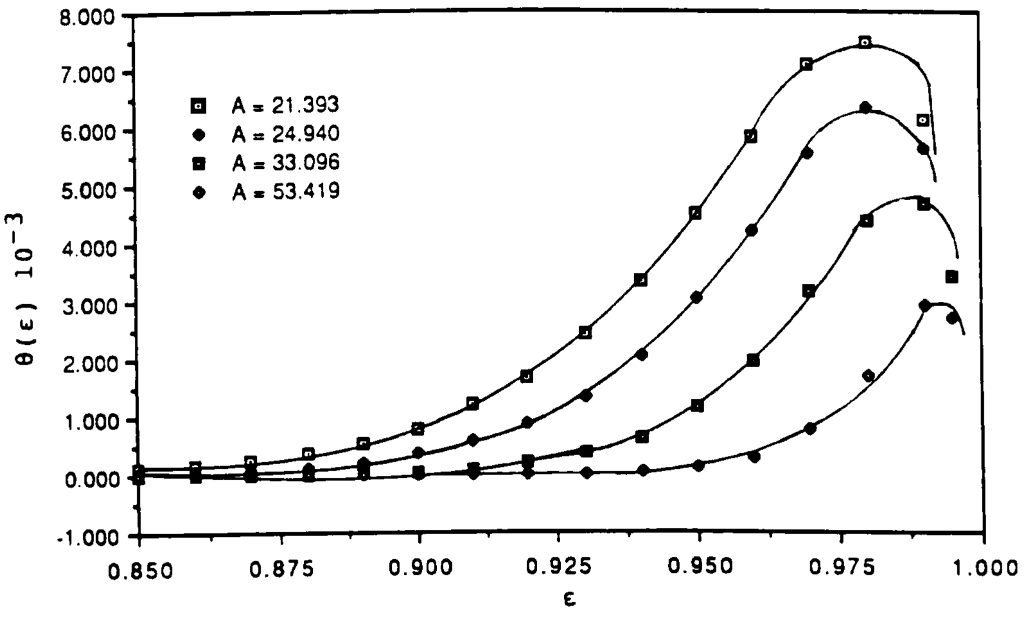

Figure 6: Plot of θ(ε) versus ε for the Kaolin NF - Tragacanth system (A = 21.39); Kaolin NF - polyvinylpyrollidone system (A = 53.42); and other systems investigated in this study.

Plots of log Q against log (ε) establish this relationship. The value of n calculated in this manner is given in Table 7. It can be seen that a relationship is clearly established between A and n, namely:

$$n = 2.15 \quad A \qquad \text{Eq. 9}$$

This relationship has not been demonstrated before.

It can be established on a theoretical basis as follows. It has been noted that a plot of Q (1-ε) against ε goes through a maximum at some value of ε designated here as ε_1. This value is generally very high and close to the limiting value of $\varepsilon = 1$. The following initial relationship is given:

$$\frac{d\{Q\,(1-\varepsilon)\}}{d\varepsilon} = \frac{d\{V_s\,\varepsilon^n\,(1-\varepsilon)\}}{d\varepsilon} \qquad \text{Eq. 10}$$

using the Richardson and Zaki relationship (Eq. 8). This gives:

$$\frac{dQ(1-\varepsilon)}{d\varepsilon} = V_s\varepsilon^n + nV_s\varepsilon^{n-1}/(1-\varepsilon) \qquad \text{Eq. 11}$$

At the maximum of the plot,

$$V_s\,\varepsilon_1{}^n = n\,V_s\,\varepsilon_1{}^{n-1}\,(1-\varepsilon_1)$$

where $$n = \frac{\varepsilon_1}{1-\varepsilon_1} \quad \text{or} \quad \varepsilon_1 = \frac{n}{n+1} \qquad \text{Eq. 12}$$

Equation 7 shows the relationship between θ(ε) and A, when:

$$\frac{d\{\log\theta\,(\varepsilon)\}}{d\varepsilon} = \frac{d[\log\{(1-\varepsilon)/\varepsilon]}{d\varepsilon} = \frac{d\{A(1-\varepsilon)\}}{d\varepsilon}$$

$$= \frac{-0.4343\ (1/\varepsilon^2)}{(1/\varepsilon\ -\ 1)} + A$$

$$= \frac{0.4343}{\varepsilon\ (\varepsilon\ -\ 1)} + A \qquad \text{Eq.13}$$

The plot of θ(ε) against ε is generally of the same shape as Q (1-ε) against ε. Designating the porosity at which a maximum is recorded in this plot as ε_2, then:

$$A = \frac{0.4343}{\varepsilon_2(1 - \varepsilon_2)} \qquad \text{Eq. 14}$$

Now, in most cases, $\varepsilon_2 \, \Omega \, \varepsilon_1$ and becomes more nearly equal for very high values of ε. Writing ε_1 for ε_2 in Eq. 14 and using Eq. 12, it follows that:

$$A = \left(\frac{0.4343}{\varepsilon_1{}^2}\right) n \qquad \text{Eq. 15a}$$

or

$$n = \left(\frac{\varepsilon_1{}^2}{0.4343}\right) A \qquad \text{Eq. 15b}$$

Thus, if $\varepsilon_1 = 0.90$, $n = 1.865A$; if $\varepsilon_1 = 0.95$, $\eta = 2.078A$, if $\varepsilon_1 = 0.98$; $n = 2.211A$, if $\varepsilon_1 = 0.99$, $n = 2.257A$ and in the limit at $\varepsilon_1 = 1.00$, $n = 2.303A$. The variation in the coefficient in Eq. 9 is, therefore, a consequence of the variation in ε_1 and Eq. 9 could be used to locate the maximum in the plot of $Q(1-\varepsilon)$ against ε.

The Permeability Approach

Permeability equations derived by Lea and Nurse[16] and by Rigden[17] have been used by Allison and Murray[18] to produce functions which describe sedimentation behavior. The approach outlined here is that of Davies and Dollimore[3]. The Kozeny-Carmen equation[4-7] for fluid flow through settled beds of solid particles takes the form:

$$V = \left(\frac{\varepsilon^3}{k n s^2}\right)\left(\frac{\Delta p}{L}\right) \qquad \text{Eq. 16}$$

where

V = Volume of fluid flowing through bed per sec (cm s^{-1}) total cross-section of container

V = Apparent fluid flow velocity through molecular bed.

ε = Volume of pore space per unit volume of bed, i.e., porosity.

k = Kozeny "constant" originally stated as 5.0.

n = Fluid viscosity ($\text{g cm}^{-1} \text{s}^{-1}$)

s = Particle surface area per unit bed volume (cm^{-1})

$\Delta\rho$ = Pressure difference across bed depth ($g\ cm^{-1}\ s^{2}$).

L = Bed depth (cm).

The value of s can be expressed for a bed of spheres, radius r and porosity ε. Let a bed volume V contain one sphere. The sphere volume is given by (1-ε) V and $V = 4/3\ \Pi r^3/(1-\varepsilon)$. Therefore,

$$S = \frac{4\pi r^2}{V} \quad \frac{4\pi r^2\,(1-\varepsilon)}{4/3\pi r^3}$$

$$= \frac{3\,(1-\varepsilon)}{r} \qquad \text{Eq. 17}$$

In any cubic centimeter of the bed there is an additional mass, as compared with the situation in motionless fluid of density ρ_p, due to the element of volume (1-ε) having an additional density $(\rho_s-\rho_p)$, ρ_s being the solid density. This creates a pressure difference $(1-\varepsilon)(\rho_s-\rho_p)\ g\ L$ across the bed depth and hence,

$$\frac{\Delta\rho}{L} = (1-\varepsilon)\,(\rho_s - \rho_p)\ g \qquad \text{Eq. 18}$$

where g = acceleration due to gravity =($cm\ s^{-2}$).

Substituting Eq. 17 and 18 into Eq. 16 for S and $\Delta\rho/L$ then gives:

$$V = \left(\frac{1}{k}\right)\left(\frac{\varepsilon^3}{1-\varepsilon}\right)\left(\frac{gr^2\,(\rho_s - \rho_p)}{9n}\right) \qquad \text{Eq. 19}$$

In hindered settling, the particles move under laminar flow conditions (i.e., with Reynolds number ≤ 0.02) with a measured velocity Q relative to a fixed horizontal plane, through a liquid volume, as compared with the flow of liquid at velocity V through a motionless bed; therefore V = Q. Since the Stokes Law limiting sedimentation rate V_s is given by Eq. 1, we may write:

$$Q = \left(\frac{1}{2k}\right)\ \left(\frac{\varepsilon^3}{1-\varepsilon}\right) \qquad \text{Eq. 20}$$

This is the form of the Kozeny-Carmen equation reported by Happel[19] as being applied to sedimentation problems. Gaudin and Fuerstenau[20] and Gaudin et al[21] have shown that this initial porosity (ε) is maintained in the sedimenting "plug" moving at velocity Q during the hindered settling. Davis and Dollimore concluded from this and associated evidence that a hindered settling plug is essentially the same as a fluidized bed and Eq. 20 describes the flow of liquid through this plug. Rearrangement of this equation gives:

$$Q(1-\varepsilon) = \left(\frac{1}{2k}\right) V_s \varepsilon^3$$

$$Q(1-\varepsilon) = \text{constant } \varepsilon^3 \qquad \text{Eq. 21}$$

if k is a constant.

It has already been explained that although complete data of $Q(1-\varepsilon)$ against ε should go through a maximum in practice all the experimental data in any one investigated system may show only a portion of this complete behavior. If, however, the data does through a maximum, then Eq. 21 implies that k must go through a minimum value at some value of porosity. The maximum in the plot of $Q(1-\varepsilon)$ against ε occurs at a porosity ε_1. It can be shown that k varies with ε to a minimum value ε_k which is less than ε_1. Use of Eq. 8 with Eq. 20 gives:

$$k = \left(\frac{1}{2\varepsilon^{n-3}(1-\varepsilon)}\right) \qquad \text{Eq. 22}$$

If the minimum value of k occurs at an initial porosity ε_k, where dk/dt = 0, then for any system obeying Eq. 22, we have:

$$\left(\frac{dk}{dt}\right) = (0.5\ \varepsilon^{3-n})(1-\varepsilon)^{-2} - 0.5(1-\varepsilon)^{-1}(n-3)\ \varepsilon^{2-n} \qquad \text{Eq. 23}$$

At the point where dk/dt = 0, $\varepsilon = \varepsilon_k$ and then Eq. 23 becomes:

$$\varepsilon_k = (n-3)(1-\varepsilon_k) \qquad \text{Eq. 24}$$

Table 8

Values of ε_1, k_{min} and ε_k for the Various Kaolin Systems.

Suspended Material	Flocculant	ε_1	k_{min}	ε_k
Kaolin NF	Tragacanth	0.980	62.95	0.978
	Polyvinylpyrollidone	0.992	164.04	0.992
Georgia Kaolin	Tragacanth	0.983	76.73	0.982
	Polyvinylpyrollidone	0.983	78.79	0.981
	Secofloc 650	0.963	33.35	0.958
	Secofloc 630	0.965	35.42	0.961
	Secofloc 611	0.936	17.88	0.921
	Secofloc 430	0.982	72.10	0.981
	Floxan EA4443	0.961	31.48	0.956
	Floxan SC 5010	0.969	40.51	0.966
	Floxan SC 5080	0.967	37.85	0.963
	Agefloc WT 40	0.985	87.29	0.984
	Agefloc A 50	0.959	29.80	0.953

Table 9

Variation of the Porosity ε_k, At Which the Minimum Value of the Kozeny Parameter Occurs With the Porosity ε_1, Corresponding to Maximum Sedimentation Mass Transfer Rate, Together with the Value of Richardson and Zaki Parameter n.

ε_1	ε_k	n	k_{min}
0.99	0.99	99	131.22
0.95	0.94	19	22.42
0.90	0.86	9	8.83
0.80	0.50	4	2.00
0.75	0.00	3	0.00
0.70	-2.00	2.33	---
0.60	+3.00	1.5	---
0.50	+2.00	1.0	---
0.25	+1.60	0.333	---

There is however, the relationship developed between n and ε_1 (Eq. 12), which allows ε_k to be expressed in terms of ε_1. We have:

$$n = \frac{\varepsilon_1}{(1-\varepsilon_1)} \frac{\varepsilon_k}{(1-\varepsilon_k)} + 3 \qquad \text{Eq. 25}$$

Rearrangement then gives:

$$\varepsilon_k = \frac{n-3}{n-2} \qquad \text{Eq. 26}$$

or

$$\varepsilon_k = \frac{4\ (\varepsilon_1-3)}{3\ (\varepsilon_1-2)} \qquad \text{Eq. 27}$$

Table 8 gives values of ε_1, k_{min} and ε_k calculated for the kaolin systems studied here. Table 9 shows how ε_k and ε_1 vary with n and the value of k_{min} at the indicated values of ε_k.

It is seen that ε_k and ε_1 are identical at values of $\varepsilon_1 > 0.95$. In these regions n is very large. We have:

$$\frac{Q_\varepsilon}{V_s} = \varepsilon_1{}^n \qquad \text{Eq. 28}$$

Using Eq. 12 gives

$$\frac{Q_\varepsilon}{V_s} = \left(\frac{n}{n+1}\right) = \left(1+\frac{1}{n}\right)^{-n} \qquad \text{Eq. 29}$$

When n is indefinitely large:

$$\frac{Q_\varepsilon}{V_s} = e^{-1} = 0.3679 \qquad \text{Eq. 30}$$

Values of n which are large correspond to highly hindered systems. It can be seen that for such systems, k_{min} is large, ε_1 and ε_k are approximately equal and close to unity. However, when hindrance is small ($n \leq 3$), these calculations are not real. In the range $0.750 < \varepsilon_1 < 0.667$, the values of ε_k are negative, and beyond this range the values of ε_k are not real. However, in all the studies reported here (see Tables 7 and 8), n is always greater than 14, ε_1 greater then 0.036, ε_k greater than 0.921 and k_{min} is always greater than 17. It is apparent that there are lower experimental limits relating to n, ε_1, ε_k and k_{min} when the above relationships are applied to real systems.

CONCLUSIONS

Aqueous suspensions of kaolin can be flocculated with a variety of flocculant molecules, and when too much flocculant is used, the system is stabilized.

The application of theories of hindered settling represented as a modification to Stokes Law results in a correlation between the parameter A, used as a characterization constant in Steinoir's empirical relationship (Eq. 6) and the Richardson and Zaki exponent n (see Eq. 8). A theoretical justification for this relationship is advanced.

The permeability relationships introduced by Davies and Dollimore have been applied here to well characterized flocculated systems for the first time and found to apply. In general the values of the ε_k and k_{min} found in the systems correspond to high n values and some show very high hindrance ($n > 50$).

The permeability treatment is based on the Kozeny-Carmen permeability equation and the variable k is shown theoretically and in practice to have a minimum value at some value of porosity determined by the nature of the concentrated suspension.

These conclusions should provide a basic fundamental characterization for simple flocculated suspensions which can provide a basis for future studies of more complex pharmaceutical preparations.

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