Sedimentation Kinetics of Flocculated Suspensions I: Initial Sedimentation Region

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Abstract ☐ Depending on the concentration of a suspension, it will exhibit one of three sedimentation patterns pertaining to low, intermediate, and high concentrations of solids, respectively. Of these, only the dilute region has been thoroughly investigated in the past from a theoretical and experimental standpoint. Pharmaceutical suspensions are mostly of the intermediate type. It is shown here that if the models by Kynch, Michaels, and Bolger pertain, and if the sedimented cake experiences an exponential compaction from the onset, experimental data are consistent with theory and lead to the relation: $x = x_0 \exp[-kt] + C \cdot [1 - \exp(-kt)] \cdot \exp[-\omega t]$, where k is a sedimentation rate constant pertaining to a constant density plug, and ω is a sedimentation rate constant pertaining to the cake. It has also been found that, empirically, the sedimentation heights in the initial stage may be presented by the relation: $[x_0^2 - x^2] = \beta t$, where x denotes height, and t time.

Keyphrases ☐ Sedimentation kinetics—flocculated suspensions ☐ Kinetic equations—suspension sedimentation ☐ Suspensions, flocculated—sedimentation cakes ☐ Viscosity effect—suspension cake concentrations

Stokes's law has been known for over a century (1) but, nevertheless, as pointed out by Kynch (2), a satisfactory theory of sedimentation of multiparticle, coarse suspensions has never been put forth. Although it might appear that sedimentation should follow Stokes's law, Higuchi (3) and Hiestand (4) have shown that both in peptized and flocculated systems such a simple point of view is in agreement with neither theory nor fact. In most of the investigations reported in the past, attempts have been made to modify Stokes's law in some way (5–9) to account for sedimentation behaviors. The more dilute a suspension is, the more closely should the fall of each particle or floc adhere to Stokes's law. Pharmaceutical suspensions are, however, rarely very dilute, and their behavior would not be expected to fall in this category.

Michaels and Bolger (10) have reported a linear pattern for sedimentation rates for dilute suspensions (<1%). These authors, as well as Haines and Martin (7), point to the fact that very concentrated suspensions follow yet another pattern, a fact that will not be a point of discussion here but will be reserved for a subsequent study (11). Suspensions of "intermediate" concentration, however, have a downward curvature, i.e., the sedimentation boundary moves downward with greater and greater velocity until a certain critical height, H_0, is reached, at which time (t_0) the rate decreases abruptly.

Examples of this pattern may be found described occasionally in pharmaceutical literature, the work by Benedict et al. (12) being an example. Pharmaceutical suspensions are mostly of the intermediate type. They, also, are of the floc-aggregate type described by Michaels and Bolger (10), and the considerations in the following apply to this type system.

Robinson (8) considered the sediment to be of uniformly increasing concentration during the descent of the boundary; Ward and Kammermeyer (9) showed that the ensuing equations apply only to special systems. Michaels and Bolger (10) and Gaudin and Fuerstenau (13, 14) have, furthermore, demonstrated that the density of the sediment remains constant at and for some (time-dependent) distance below the boundary, with a cake of higher density building up at the bottom, and that, therefore, the system is uniform at time zero only. The terms cake and sediment will be used for these two phases in the following. These views correlate with the simplest of the models proposed by Kynch (2).

From a pharmaceutical point of view, it is important to determine the pattern (and predict ultimate heights) of suspension sedimentation. It is one of the objectives of this communication to establish graphical means of describing the descent of the sedimentation boundary in the initial stage, i.e., prior to the critical height, H_0. Another objective is to attempt to correlate the initial sedimentation pattern with existing views on the sedimentation process and arrive at a general equation for the initial sedimentation of flocculated suspensions in the intermediate concentration range.

EXPERIMENTAL

The system used here is the same as that employed by Michaels and Bolger (10) except that concentrations are higher. At higher concentrations, air entrapment might be a source of variation, and an apparatus such as shown in Fig. 1 was used. Previous investigators of dilute suspensions (8) have pointed out that initial turbulence was a source of variation, without spelling out the extent of this variation. The method of providing a uniform starting suspension used here was the same as that employed by Michaels and Bolger (10) (turning the tube end-over-end 10 times). This, of course, causes initial turbulence; the extent to which this affected results was gauged by performing each experiment at least three times.

The size of aggregates is a dynamic property and forming the aggregate under high shear (Waring blender) will not necessarily give a representative floc-aggregate (10) in the sense that the size will subsequently remain constant during settling. Some experiments were, therefore, conducted by allowing a mildly agitated suspension to equilibrate. The sedimentation experiment was repeated until the curves were reproducible. This appeared to require about 24 hr. Reproducible curves all show the convexity noted in the top curve of Fig. 2. Where suspensions were made in a blender, they were also checked on succesive days until the sedimentation rates had changed to a constant value.

The general procedure used, then, was as follows: 25 g. of colloidal kaolin NF[1] was rinsed with 500 ml. of water which had previously been distilled over potassium permanganate. The volume was then adjusted to 500 ml. and the suspension transferred to a tube of the type shown in Fig. 1. The suspension was thoroughly deaerated by applying aspirator vacuum to one of the outlets of the two-way stopcock. The tube was occasionally turned end-over-end, and finally after no more visible escape of air, the tube was turned end-over-end 10 times, then opened to the atmosphere and placed vertically; the movement of the interface was followed by use of a high precision cathetometer[2] and an electric timer. After 24 hr., the

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[1] Merck and Co., Log No. 781603-62325, Rahway, N. J.
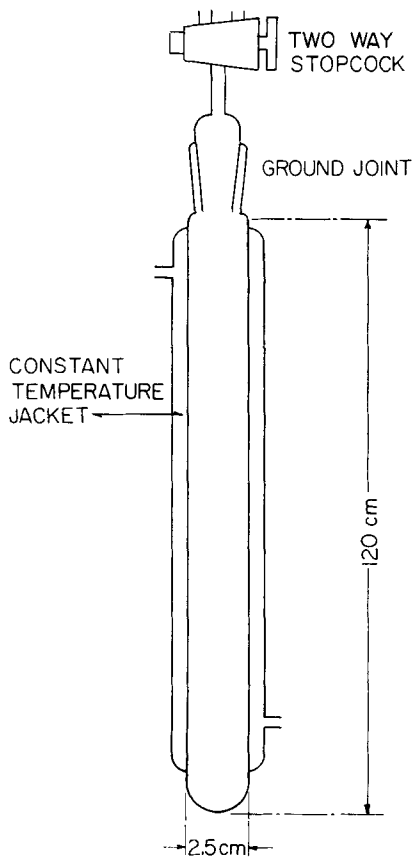[2] Gaertner Scientific Corp., Chicago, Ill.

Figure 1—*Apparatus set-up for sedimentation studies.*

Figure 3—*Sedimentation curves in 10% v/v glycerin in water at various temperatures. The temperature was varied from experiment to experiment as a means of varying the viscosity.*

tube was again evacuated, turned end-over-end 10 times, opened to the atmosphere, and the procedure carried out again. This was then repeated until three successive, reproducible curves were obtained.

Part of the supernatant was then replaced by an equal volume of glycerin and the procedure repeated. Data were obtained at four glycerin concentrations; at each point where supernatant was replaced by glycerin, the viscosity of the supernatant was checked by means of an Ostwald-Fenske viscometer. All experiments were carried out in a constant-temperature room (25 ± 0.3°). In one set of experiments, lower (constant) temperatures were obtained by circulating constant temperature water through the jacket of the tube. It should be noted that the apparatus cannot be insulated and that good temperature control throughout the length of the tube is only possible at temperatures less than 5° above or below the temperature of the surrounding area.

A note on some visual manifestations may be in order here. The interface is well defined and horizontal during the free-fall period. When the point of transition into the second, slower phase of the sedimentation is approached, a fairly heavy concentration of fine particles appears above the interface for a short while. At the critical time t_0, which is reproducible to within 5%, the surface suddenly becomes ragged, and at that particular time the second phase starts. The patterns associated with the second phase are the subject of a separately reported study (11). A set of runs was performed at 7, 9, and 11% by weight of kaolin in water as well.

RESULTS AND DISCUSSION

All of the tested systems showed convex curvature in the initial phase, such as shown in Figs. 2 and 3. This evidently differs from the linearity exhibited by more dilute systems.

If the sedimentation patterns found here for flocculated suspensions in the intermediate concentration range are analogous to those suggested for dilute systems by Kynch (2), Michaels and Bolger (10), and Gaudin and Fuerstenau (13–15), then, at time t, there will be a-centimeters of suspension containing the initial volume fraction ϕ_0 of solids, and b-centimeters of suspension containing the volume fraction in the cake (ϕ). The height of the sediment will be $x = a + b$. As time progresses, a will diminish at the expense of b. The a-values deduced from the data by Michaels and Bolger (Fig. 6, *Reference 10*) are reproduced in Fig. 4, and it is seen that an equation of the form $a = x_0 \exp [-kt]$ is a good fit. The decrease in a may, therefore, be considered to be of the form:
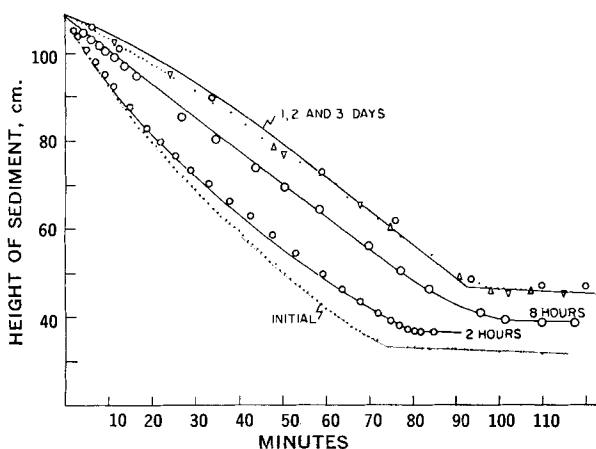
$$a = x_0 \exp [-kt] \qquad \text{(Eq. 1)}$$

Figure 2—*Sedimentation curves in water as a function of time of a suspension made at low shear. Triangles and small circles by the upper curve are points from different runs.*
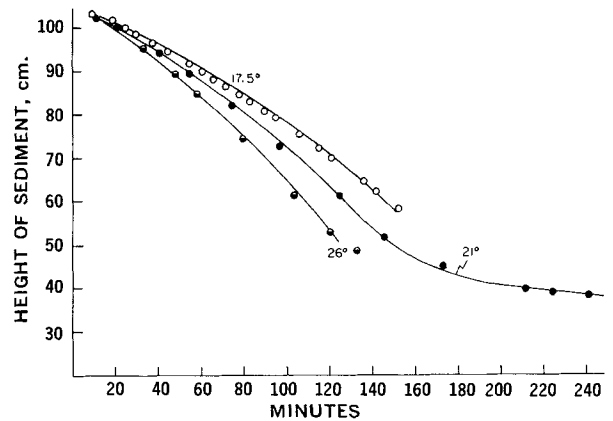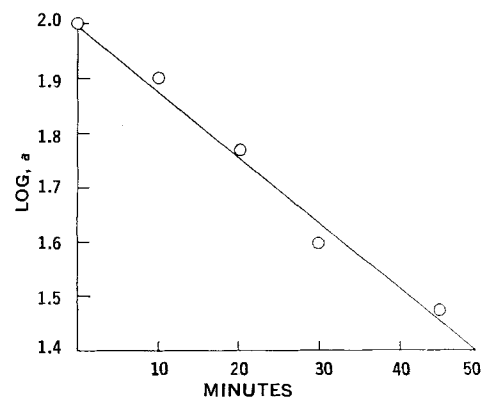

Figure 4—*The graph shows the result of logarithmic treatment of data reported by Michaels and Bolger (10). If the logarithm of the length of the constant-density plug is plotted as a function of time, then a straight line results, as shown in the plotting used here. The data refer to a 1.9% calcium oxide suspension.*
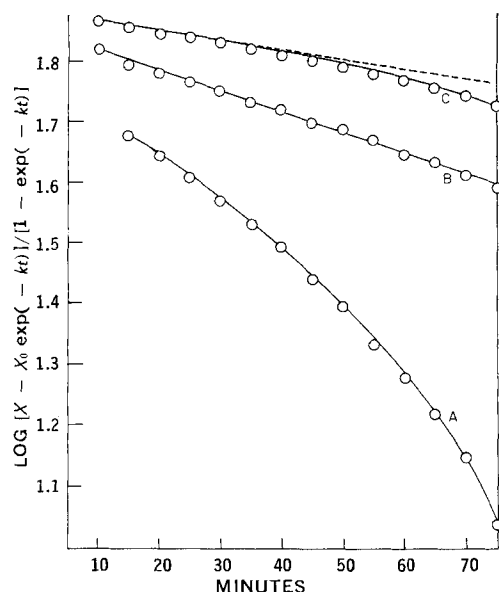
Figure 5—*Sedimentation data from a 7% by weight kaolin suspension plotted according to Eq. 7, using three values of k. Key: Curve A, k = 0.005 min.$^{-1}$; Curve B, k = 0.01 min.$^{-1}$; Curve C, k = 0.025 min.$^{-1}$. Temperature: 28°.*

To describe the time dependence of x, it is necessary to know how b changes with time. It has been shown (11, 16) that the cake (in the final phase) experiences an exponential decay, so $db/dt = -\omega \cdot b$. In the initial phase, it also experiences a build-up from the temporal contribution of the sediment. If the cross-sectional area is denoted Q, then the amount of solids in the cake at time t is $b \cdot Q \cdot \phi$; the amount of solids in the suspension above the cake is $Q \cdot a \cdot \phi_0$ (since it contains the initial volume fraction of solids). The original amount of solids was $x_0 \cdot Q \cdot \phi_0$, so material balance dictates that $Q \cdot a \cdot \phi_0 + b \cdot Q \cdot \phi = x_0 \cdot \phi_0 \cdot Q$, or $a \cdot \phi_0 + b \cdot \phi = x_0 \cdot \phi_0$. This may be rewritten:

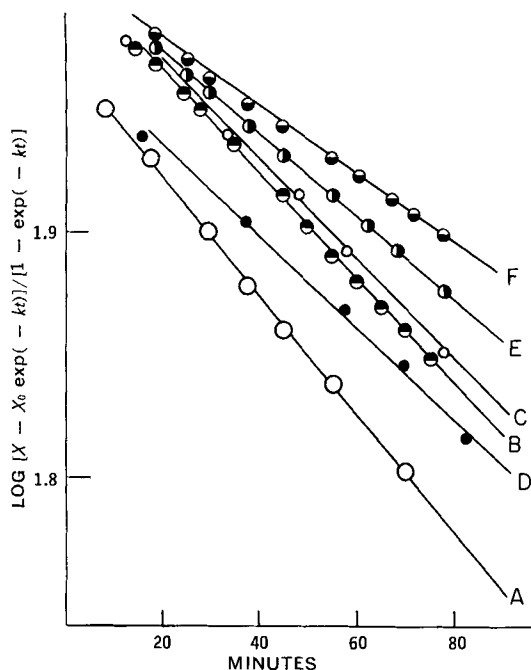$$\phi = \frac{[x_0 - a] \cdot \phi_0}{b} \quad \text{(Eq. 2)}$$

Figure 6—*Sedimentation data from 5% kaolin suspensions in aqueous glycerin vehicles, plotted according to Eq. 7. Curve notations are shown in Table I, indicating the employed k-values and the viscosity corresponding to each line.*

Table I—*k*- and ω-Values at Various Viscosities

Curve in Fig. 6	Viscosity, cps.	Rate Constant k, min.$^{-1}$, $\pm 10^{-3}$	Compaction Constant ω, min.$^{-1}$, $\pm 10^{-4}$
A	0.87	0.035	0.0055
B	0.96	0.032	0.0049
C	1.12	0.028	0.0046
D	1.19	0.024	0.0046
E	1.35	0.023	0.0039
F	1.40	0.022	0.0032
	2.40	0.013	0.0023

The total change of b with time, then, is:

$$\frac{db}{dt} = \frac{k \cdot \phi_0 \cdot a}{\phi} - \omega \cdot b \quad \text{(Eq. 3)}$$

Inserting Eqs. 1 and 2 into Eq. 3 yields:

$$\frac{db}{dt} = k \cdot \frac{\exp[-kt]}{1 - \exp[-kt]} \cdot b - \omega \cdot b \quad \text{(Eq. 4)}$$

which has the solution:

$$b = C \cdot \{1 - \exp[-kt]\} \cdot \exp[-\omega t] \quad \text{(Eq. 5)}$$

The expression for $x = a + b$, then is:

$$x = x_0 \exp[-kt] + C \cdot \{1 - \exp[-kt]\} \cdot \exp[-\omega t] \quad \text{(Eq. 6)}$$

For the purpose of plotting, this is rearranged:

$$\log\left(\frac{x - x_0 \exp[-kt]}{1 - \exp[-kt]}\right) = -\frac{\omega}{2.3} \cdot t + \log C \quad \text{(Eq. 7)}$$

The data may now be plotted using estimates of k,[3] and by applying successive values of k, a best k-value (*i.e.*, the k-value that imparts linearity[4] to the data when treated according to Eq. 7) can be arrived at. An example of this is shown in Fig. 5. If done manually, two or three k-values are arrived at (*e.g.*, 0.034, 0.035, and 0.036 min.$^{-1}$) which produce lines without apparent curvature. The value giving the best statistical fit (17, 18) is then chosen. With the aid of a computer, the iteration procedure can be accomplished rapidly. Figure 6 and Table I show data at various viscosities plotted according to Eq. 7. With the proper k-value, linearity prevails to within 15 cm. of the critical height.

The dependency of k on the viscosity is of interest, and Fig. 7 shows that the logarithm of the rate constant is linearly related to the logarithm of the viscosity. The slope is reasonably close to minus unity, so that k is inversely proportional to viscosity. This type behavior might suggest that Stokes's law, with some modification, applies, since the stokes velocity is also inversely proportional to viscosity. In a suspension, the forces involved are both of van der Waals and electrical nature (15, 19–23). In causing flocculation they might be playing a part directly in the sedimentation process, *i.e.*, the rate constant might be associated with a flocculation rate. By such a visualization, the initial perturbance causes an equilibrium floc, A_j (containing on the average j single particles) to be broken up into smaller flocs, A_i. This, of course, is a highly simplified picture, because $A_j \rightarrow A_i$ could not be a single-step process. Furthermore, both i and j would present averages of a population of numbers.

It would also have to be assumed that A_j, once formed, would appear immediately in the cake; in spite of these shortcomings, the viewpoint explains the inverse relationship between rate constant and viscosity, and can not be eliminated as a possibility. W. Higuchi *et al.* (24, 25) have shown that k_{ij} approaches some factor times k_{11}, the rate constant for combination of single particles, and have also shown that $k_{11} = 8k_0T/3\eta$. It is not possible to test this hypothesis on more concentrated systems with the data presented here;

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[3] First estimates of k (and ω) can be obtained from Eq. 6 by feathering technique if k and ω are not of the same order of magnitude.

[4] The value giving the best statistical fit (17, 18), *i.e.*, the one producing the least residual sum of squares.
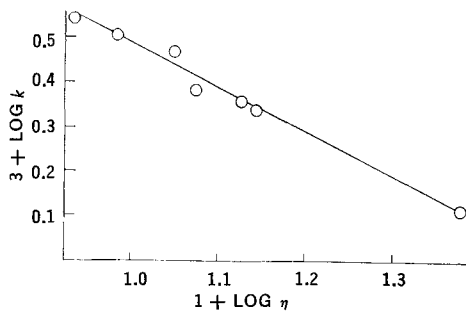
Figure 7—*A plot of the logarithm of the rate constant* k *versus the logarithm of the viscosity. The drawn line has a slope of minus unity:* k *is in units min.*$^{-1}$ *and viscosity is in cps.*

to such an end it would be necessary to perform experiments where the initial perturbance (deflocculation) could be varied in a quantitative way. Experimental procedures in previous publications as well as this work have simply been designed to achieve a reproducible perturbance, so that data are comparable; it may be, for the reasons quoted, that data may not be comparable from author to author.

The values of ω are obtained from the slopes in Fig. 6 and are listed in Table I. The values are plotted as a function of viscosity in Fig. 8. The general range of the ω-values is in good agreement with data on cake contraction reported by Carstensen and Su (11) who found ω_1-values in the range of 0.2–0.4 hr.$^{-1}$ (*i.e.*, 0.003–0.007 min.$^{-1}$). It would appear from Fig. 8 that ω is inversely proportional to the viscosity.

At higher concentrations the critical height, H_0, increases and the curves show less distinct breaks. Evaluation of data by Eq. 7 becomes less exacting, and k values are at best ±20%. The k-values seem to taper off at a value of 0.01 hr.$^{-1}$ as shown in Fig. 9, but ω-values decrease with increasing concentration.

As a last comment on the treatment of the preceding, attention should be called to the fact that an obvious approximation is made in assuming the cake to be of uniform concentration along the entire length b. However, attempts to present ϕ as a function of x lead to forms of Eq. 3 that cannot be solved analytically. That the approximation is not unrealistic is apparent both from the X-ray data by Gaudin and Fuerstenau (13, 14) and by the linearity which can be achieved by inserting proper k-values in Eq. 7. On the other hand, deviation from linearity close to the critical height undoubtedly reflects the effect of the approximation.

It is often convenient, in the laboratory, to have a rapid method available for plotting; the treatment just outlined, clearly, is not rapid. For routine plotting, the initial convex portion of the curve may be approximated by a parabola, *i.e.*, $x_0^2 - x^2 = \beta t$, where x_0 is the initial height. Data are plotted in this fashion in Figs. 10 and 11, and, with exception of the initial turbulent period (8), the data fit such a relationship well. It should be noted that this means of presentation is purely empirical, and that the comments to follow may not have general applicability but may merely apply to the kaolin-glycerin-water system. The value of this type of practical approach
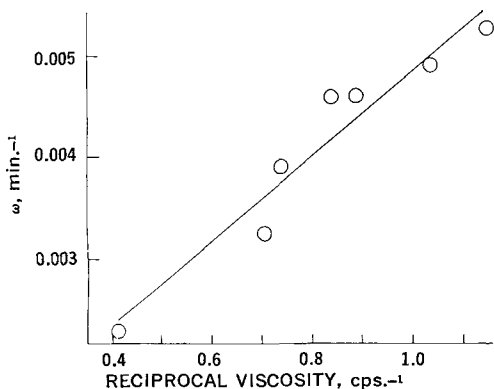

Figure 8—*A plot of the compaction-rate constant,* ω, *versus reciprocal viscosity.*
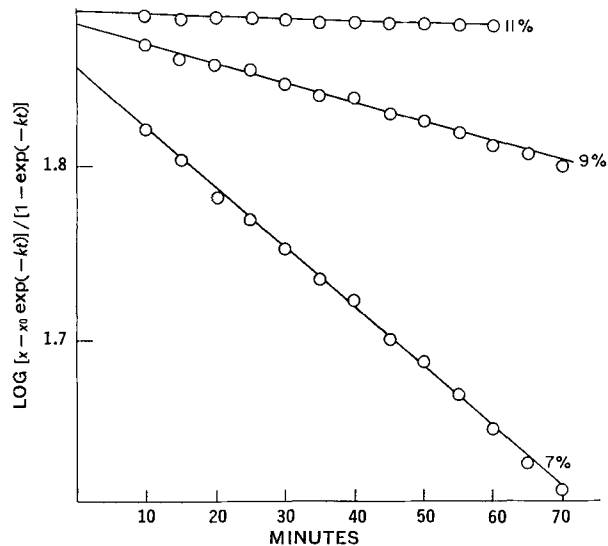
Figure 9—*Sedimentation data from* 7, 9, *and* 11% *kaolin suspensions in water, plotted according to Eq.* 7, *all using a* k-*estimate of* 0.01 min.$^{-1}$.

is that it allows rapid extrapolation and implies at what time the critical height is being approached.

Analogies have been made in the past (26) between the fall of the boundary to the flow of liquid through a porous plug in an infinitely long medium. By applying the Poiseiuille equation[5] such a view would require that $V/t = \pi P r^4/8L\eta$, where V/t is volume flow per unit time, P is pressure head, r is a capillary radius parameter, and L is the length of the plug. Since each milliliter flowing through the plug is associated with a height decrease of $1/\pi R^2$, the velocity of the interface would be: $V/(t\pi R^2) = (Pr^4)/(8L\eta R^2) = \beta/(2.L) = (dx)/(dt)$, where R is the radius of the tube and the sedimentation constant $\beta = Pr^4/4\eta R^2$. If L approximately equals x, a formal integration would yield $x^2 - x_0^2 = -\beta t$, assuming the pressure head to be constant. This is not theoretically justifiable. Although, as required by the treatment, the sedimentation constant appears to be inversely proportional to the viscosity, it should also be inversely proportional to R^2; data reported elsewhere (11) show this not to be the case. The squared-heights fitting is, therefore, only empirical.
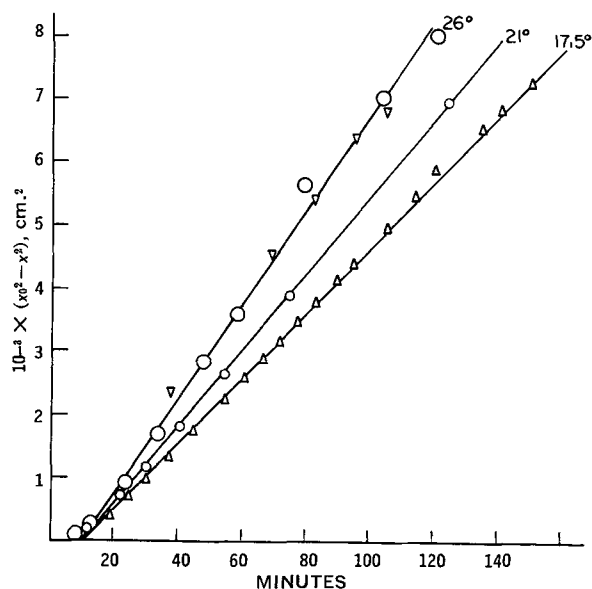
Figure 10—*Squared-heights curves for* 5% *kaolin suspensions in* 10% v/v *glycerin in water at three temperatures.*

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[5] Use of the Kozeny-Carmen equation (27, 28) does not change the consequences of the arguments outlined.
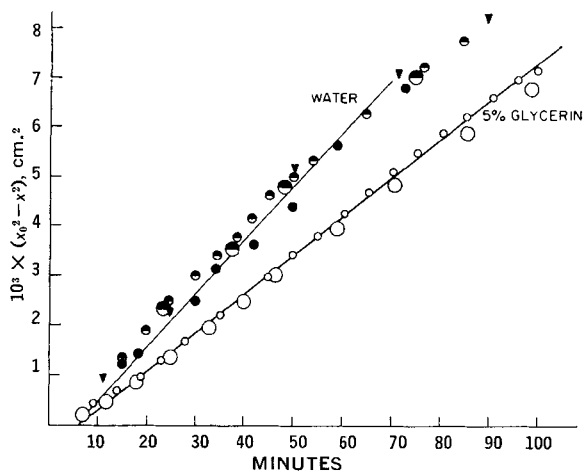
Figure 11—*Squared-heights curves for 5% kaolin suspensions in water and 5% v/v glycerin in water.*

SUMMARY

By assuming the sedimentation process to consist of the descent of a constant density plug and simultaneous build-up of a higher density cake, it has been shown that sedimentation data are consistent with theory, if it is assumed that the exponential contraction of the cake is initiated at zero time. The point in time, t_0, the critical time, where the boundary of the sediment and the cake coincide, denotes the end of the initial stage of sedimentation.

Empirically, sedimentation data in the initial stage are amenable to plotting by graphing the square of the height as a function of time. The slope of these lines appears to be proportional to the ratio of density difference to viscosity.

NOMENCLATURE

a = length of sediment (cm.) (constant-density plug).
b = height of cake (cm.).
C = preexponential factor for cake contraction (cm.).
H_0 = critical height (cm.) at which point the first phase of sedimentation ends and the second phase starts.
k = rate constant for sediment (min.$^{-1}$).
L = length of constant-density plug falling through infinitely long column of liquid (cm.).
P = pressure head (dynes/cm.^{2}).
R = radius of tube (cm.).
t_0 = time at which H_0 occurs; critical time (min.).
V = volume (cm.^{3}).
x = height of sediment interface above bottom of tube (cm.).
x_0 = initial height (cm.).
β = sedimentation constant (cm.^{2}/min.).
η = viscosity, centipoise or poise, as indicated.
ϕ = volume fraction of suspended matter in cake.
ϕ_0 = volume fraction of suspended matter in sediment.

ω = compaction rate constant (min.$^{-1}$), *i.e.*, exponential decay constant for cake height.

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