

Sedimentation Kinetics of Flocculated Suspensions III: Effect of ζ -Potential

J. THURØ CARSTENSEN[▲], KENNETH P. STREMMING, and PAKDEE POTHISIRI

Abstract □ The sedimentation of flocculated suspensions in an intermediate concentration range was previously shown to consist of an initial region of pseudoparabolic nature and of a final region of biexponential character. The rate constant, k , of the initial region is shown here to be a function of both Stokes and aggregational forces, and a method is outlined showing the effect of both. The electrical potential effect on the sedimentation kinetics was studied by varying the ζ -potential; of the contraction rate constants, ω_1 and ω_2 , in the final region, the larger (ω_1) is fairly independent of the ζ -potential whereas the reciprocal of ω_2 is linearly related to the reciprocal of the ζ -potential.

Keyphrases □ Zeta-potential—effect on sedimentation kinetics of flocculated suspensions □ Flocculated suspensions, sedimentation kinetics—effect of ζ -potential □ Sedimentation kinetics—flocculated suspensions, effect of ζ -potential

The sedimentation patterns of flocculated suspensions were the subjects of two previous publications (1, 2). In the intermediate concentration range, the sedimentation height *versus* time curve consists of two regions; the initial region is governed by floc-aggregate size and aggregation kinetics (1), and the final phase is dictated by the effect of physical factors on the contraction of the bed of the equilibrium floc-aggregate (2). The equations for the height (x) as a function of time (t) for the two regions are:

$$x = x_0 \cdot \exp(-kt) + C \cdot [1 - \exp(-kt)] \cdot \exp(-\omega_1 t) \quad (\text{Eq. 1})$$

and:

$$x - H_u = A_1 \cdot \exp(-\omega_1 \tau) + A_2 \cdot \exp(-\omega_2 \tau) \quad (\text{Eq. 2})$$

where x_0 and H_u are initial and final heights of sediment, respectively; k is the conversion constant from the non-equilibrium to the equilibrium floc-aggregate; the critical height, $A_1 + A_2$, occurs at time $t = t_c$; and the

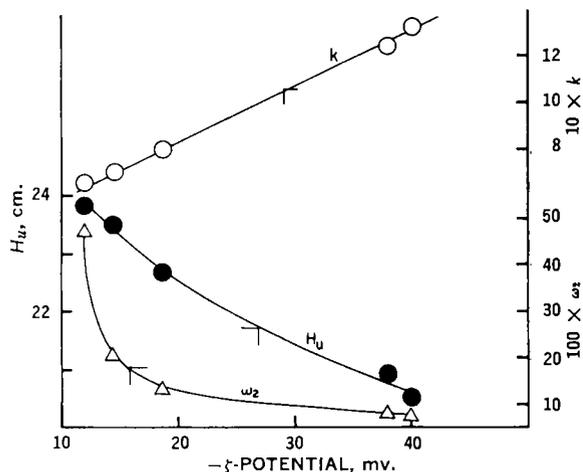


Figure 1—Initial sedimentation rate constant (k), second contraction rate constant (ω_2), and final height (H_u) as a function of ζ -potential.

second phase is measured from this point on, *i.e.*, $\tau = t - t_c$. It has been shown (2) that the ω_1 found from the final sedimentation phase equals that for the initial phase. Equation 2 was derived theoretically considering frictional, gravitational, and electrical forces; the effects of the former two have been elucidated (2) but that of the latter have not. In the derivation leading to Eq. 2, the electrical forces were assumed to be of the larger magnitude the lower the sedimentation interface (*i.e.*, the more closely the bed was packed). The repulsion term was assumed to be $\Phi = \theta \cdot [H_0 - (x/2)]$, *i.e.*, the smaller x , the larger Φ . It was shown that ω_1 is independent of θ :

$$\omega_1 = \frac{B}{M} \quad (\text{Eq. 3})$$

but that ω_2 is proportional to θ :

$$\omega_2 = \frac{\theta}{B} \quad (\text{Eq. 4})$$

where B is frictional force function, and M is the mass of sediment.

The θ can be varied by varying the ζ -potential of the system, and the intent of this study is to elucidate the effects of the ζ -potential on sedimentation kinetics.

EXPERIMENTAL AND RESULTS

A previously described experimental setup (1, 2) was used for the sedimentation studies; the tube used was 2.46 cm. in diameter. The suspensions tested were 25% (w/v) suspensions of 5- μ silica¹. This is an air-separated, natural silica. The maximum size particle is 5 μ in length, and the average size is 1 μ (3); the size distribution is quite narrow. Several batches of this product were tested, and reproducibility of sedimentation patterns was only possible by washing the silica with dilute hydrochloric acid. The following general procedure gave reproducible sedimentation patterns and was used for all systems described here.

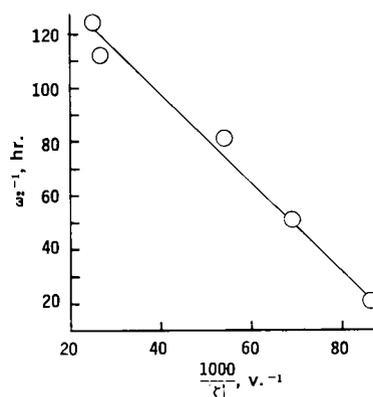


Figure 2— $1/\omega_2$ as a function of $1/\zeta$.

¹ Min-U-Sil, Pennsylvania Glass and Sand Corp., Pittsburgh, Pa.

Table I—Sedimentation Parameters at Various ζ -Potentials

Electrolyte	Concentration, mM	ζ -Potential, mv.	Sedimentation Rate Constants, hr. ⁻¹			Final Height, H _u , cm.
			<i>k</i>	ω_1	ω_2	
Calcium chloride	3.00	-12.0	0.052	0.0065	0.0450	23.82
Calcium chloride	1.50	-14.5	0.065	0.0070	0.0186	23.45
Calcium chloride	0.75	-18.3	0.08	0.0075	0.0116	22.665
Sodium chloride	0.5	-38.1	0.125	0.0056	0.0088	21.93
Sodium chloride	1.0	-40.0	0.132	0.0064	0.0080	20.50
Sodium chloride	2.5	-40.0	0.132	0.0064	0.0080	20.555

Silica, 121 g., was suspended in water, adjusted to 485 ml. total volume with water, and sheared for 5 min. in a blender (Waring). Then 1 ml. of concentrated hydrochloric acid was added, and the suspension was transferred to a sedimentation tube. After 12 hr. the supernate was siphoned off, and 500 ml. of distilled water was added. The suspension was then shaken, the supernate was siphoned off, etc., until the silica had been washed five times. After the last decantation, the suspension was brought to a volume of 484 ml. with water and 242 ml. of 0.1% (w/v) aqueous methyl *p*-hydroxybenzoate solution, so that the solution was 0.05% with respect to the preservative. The preservative was incorporated because long periods (3 months) were necessary to attain the final height. The systems were such that they could not be tested at 0% electrolyte concentration since a clear interface was not formed; small amounts of sodium and calcium chloride, however, leave the supernate clear. These two substances were used to adjust the ζ -potential².

Sedimentation patterns such as were described earlier (1, 2) were obtained; the results are listed in Table I. The *k* and ω_1 values were obtained *via* iteration procedures as described earlier (1) and ω_2 values from the biexponential final curve (2).

DISCUSSION

Linearity appears to result when *k* is plotted *versus* ζ -potential as shown in Fig. 1. The parameter *k* is affected both by aggregation rate and floc-aggregate size. An attempt to separate these effects is shown later (Eq. 6). The final height, H_u, is also plotted *versus* ζ -potential in Fig. 1 and demonstrates a principle reported for many other systems (5, 6)—*viz.*, that H_u is highest when the ζ -potential is closest to zero.

It is noted from Table I that ω_1 is fairly insensitive to ζ -potential as expected from Eq. 3. However, the ζ -potential has a strong effect on ω_2 , and Fig. 2 shows that for this system:

$$\frac{1}{\omega_2} = -\frac{1600}{[\zeta]} + 160 \quad (\text{Eq. 5})$$

Equation 5 is compatible with Eq. 4 in the sense that an increase in ζ -potential increases the electrical repulsion between floc-aggregates.

The effect of electrolytes on flocculation was reported by other authors (7, 8). It was pointed out earlier (1) that with respect to the initial rate constant, *k*, this might be a function of aggregation rates,

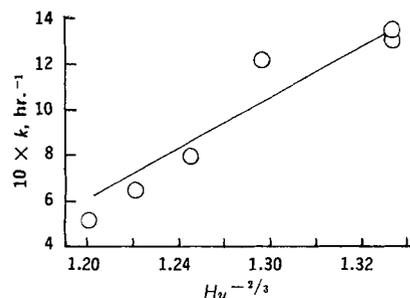


Figure 3—*k* as a function of H_u^{-2/3}.

since its viscosity dependence is of the form encountered in aggregation kinetics (9, 10). There is no doubt, however, that Stokes forces also influence the initial sedimentation phase. If *k* is considered to be a function of floc size in the sense that it depends linearly on *r*², where *r* is the "diameter" of the final floc-aggregate, and if it is also considered to depend on aggregation rates (1), then it may be put in the form:

$$k = ar^2 + b \quad (\text{Eq. 6a})$$

or:

$$r = (\alpha k + \beta)^{0.5} \quad (\text{Eq. 6b})$$

If each floc is separated on the average by *l* cm., then the number of flocs in a cross section is:

$$m = \pi(1.23)^2/l^2 \quad (\text{Eq. 7})$$

The total number of particles is:

$$N = \frac{M}{\rho} \cdot \frac{1}{4\pi r^3/3} = \frac{3M}{4\pi\rho(\alpha \cdot k + \beta)^{3/2}} \quad (\text{Eq. 8})$$

If each cross-section is *l* cm. apart, then the total number of particles is also given by H_u·*m*/*l* so that from Eqs. 7 and 8:

$$(\alpha k + \beta)^{3/2} = \frac{M \cdot 3 \cdot l^3}{H_u \cdot (1.23)^2 \cdot \pi^2 \cdot \rho} \quad (\text{Eq. 9})$$

Therefore, $\alpha k + \beta$ should be proportional to *l*² and inversely proportional to H_u^{2/3}. Figure 3 shows that the latter relationship holds fairly well; in this view, α is the component of *k* that is governed by the Stokes relation and β is the component that is governed by aggregation kinetics. It is noted from the development of Eq. 6 that *a* and *b* are positive; hence, $\beta = -b/a$ must be negative. Figure 3 shows this to be so in the system tested.

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ACKNOWLEDGMENTS AND ADDRESSES

Received June 5, 1972, from the School of Pharmacy, University of Wisconsin, Madison, WI 53706

Accepted for publication July 12, 1972.

▲ To whom inquiries should be directed.

² This was checked with both a Zetameter (4) (Zetameter Corp., New York, NY 10028) and an electrophoretic mass transport analyzer (Numenco-Numec Instruments and Controls Corp., Monroeville, PA 15146).