Particle-size Determination of Suspensions or Emulsions by Viscometry*

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The purpose of this work is to evaluate the particle-size distribution in the subsieve range of disperse systems, either suspensions or emulsions, by determining the relation between the relative viscosity of the system (η_{rel}) and the volume fraction of the particles (ϕ). The measuring apparatus is an assembly of a modified Maron-Belner-type capillary viscometer[1] and a sedimentation tube, which provides a means for the measurement of the viscosity change with time at a fixed position in the bulk resulting from the sedimentation or ascension of dispersed particles.

In addition, this method seems to be useful for the viscosity measurement of dispersions with either quickly-sedimenting or -ascending particles.

Apparatus and Theoretical

Equipment.—Figure 1 shows a sketch of the measuring apparatus, which is composed of two glass units; one is a sedimentation tube (S), and the other is essentially a capillary viscometer, consisting of a capillary tube (C) and a manometer tube (M). The two units are connected by a rubber stopper at the end of the sedimentation tube.
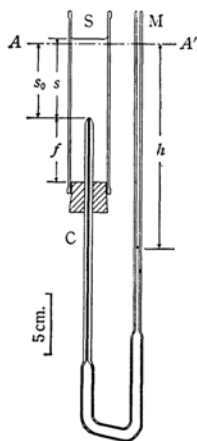

Fig. 1. Measuring apparatus.
A—·—A': Liquid level of the hydrostatic balance.

In the present study, an apparatus was employed in which the inner radii of the sedimentation tube (R_S), the capillary tube (R_C) and the manometer tube (R_m) were 1.47_8 cm., 0.0249_2 cm. and 0.304_4 cm. respectively, while the length of the capillary tube (L) was 19.90 cm. The height of the capillary in the sedimentation tube, presented as f in Fig. 1, can be changed from 0 to 10 cm. in accordance with the movements of the dispersed particles.

Although the dimensions of all the sections can be assembled interchangeably, the ratio $(R_C/R_m)^4$ must be kept in all instances below 0.004 in order to make negligible the resistance of flow in the manometer tube compared to that in the capillary tube.[1]

Operation.—The two units are joined as shown in Fig. 1 and are held vertically in place by means of a clamp. The sample is next introduced into the sedimentation tube, and the sample flows to the manometer tube through the capillary. During this flow, the times corresponding to the liquid meniscus in the manometer tube are recorded.

It may be desired that the above procedure be made in a thermostat since the viscosity changes remarkably with the temperature.

The Theory of Measurement.—The measuring apparatus is designed on the basis of a linear relationship between $\log \eta_{rel}$ and ϕ in the low dispersion concentrations.[2] Moreover, if the value of η_{rel} is measured at a fixed position in the sedimentation tube containing the dispersion, this value will decrease with time as a result of the sedimentation or ascension of dispersed particles. The decreasing curve of $\log \eta_{rel}$ against time may correspond to the cumulative curve for the volume frequency of dispersed particles against the particle sizes.

The proper selection of suspending fluid to be used depends on various factors, as has been illustrated in the ordinary sedimentation method.[3]

Typical observations obtained by using the measuring apparatus are schematically presented

1) S. H. Maron and R. J. Belner, *J. Appl. Phys.*, **26**, 1457 (1955).
2) R. Rutgers, *Rheologica Acta*, **2**, 305 (1963).
3) R. D. Cadle, "Particle Size Determination," Interscience Publisher, New York (1955), p. 202.
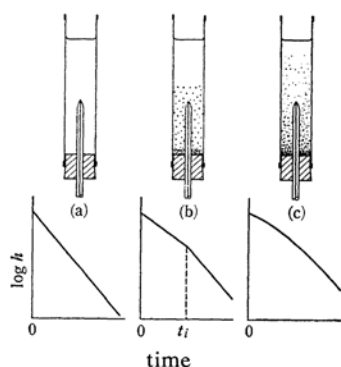
Fig. 2. Schematic curves of $\log h$ vs. time for suspending fluid (a), mono (b) and polydispersed (c) suspensions.

in Fig. 2, where h denotes the difference in the meniscus of the fluid between the manometer tube and the hydrostatic balance, as is shown in Fig. 1. In the case of a suspending medium (Newtonian fluid), $\log h$ against time reveals a linear relationship, as is shown in Fig. 2(a), while the broken line at time t_i in (b) is obtained with a monodispersed suspension. At time t_i, the boundary part between the dispersion and its suspending fluid may pass down or up to the end of the capillary tube. In the case of a polydispersed suspension, which is the most frequent case in practice, the plot of $\log h$ against time shows an upward convex curve, as may be seen in c.

In the same manner as has been established by Maron and Belner[1] for the capillary tube viscometer, the viscosity of the suspending fluid (η_0) with the present apparatus may be given by

$$\eta_0 = -\{R_c^4 \alpha/8(2.303)LR_m^2\}\rho_0/m_0 \qquad (1)$$

or

$$d\log h/dt = -m_0 = -B\rho_0/\eta_0 \qquad (2)$$

where ρ_0 is the density of the suspending fluid, m_0 is the slope of $\log h$ against time, and α and B are the constants of the apparatus, as Eqs. 3 and 4 show:

$$\alpha = g\{1+(R_m^2/R_s^2)\} \qquad (3)$$

$$B = R_c^4 \alpha/8(2.303)LR_m^2 \qquad (4)$$

where g is the gravitational constant, and R_c, R_m, R_s and L are the dimensions of the apparatus, as has been described above.

When a monodispersed suspension flows in the capillary tube, the slope of $\log h$ against time, presented as m, is smaller than m_0 and will agree with m_0 after time t_i. On the other hand, the slope of a polydispersed suspension approaches m_0 with time, so that the η_{rel} value of this system will approach unity with a decrease in the dispersion concentration. If the relation of Eq. 2 is expanded for a given

time, t, the ratio of the slope of the suspending fluid to that of the dispersion at time t should be expressed as Eq. 5:

$$m_0/m = \eta\rho_0/\eta_0\rho \simeq \eta_{rel} \propto \phi \qquad (5)$$

where η is the viscosity, ρ is the density, and ϕ is the volume fraction of dispersed particles of the system at the end of the capillary tube at time t respectively. Figure 3 shows the schematic plots of the ratio m_0/m corresponding to the times for mono- and polydispersed systems.
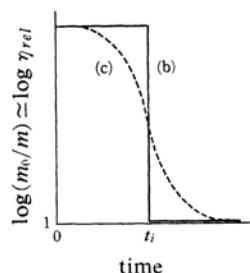

Fig. 3. Schematic curves of m_0/m vs. time for mono (b) and polydispersed (c) suspensions.

In the case of a monodispersed suspension, the time t_i corresponds to the dispersed particle size according to Stokes' equation:

$$t = 18x\eta_0/(\rho-\rho_0)gD^2 \qquad (6)$$

where D is the particle diameter, and x agrees with the distance of the sedimentation (equal to s in Fig. 1) or ascension (equal to f in Fig. 1) of dispersed particles. On the other hand, the size distribution of the particles of a polydispersed suspension may be reflected in the results over the entire measuring times; therefore, the decreasing curve c in Fig. 3 reminds us of a cumulative curve for the volume frequency of dispersed particles against the particle sizes, and of the possibility of obtaining the size distribution curve. The distribution function of the particle size frequency for the volume concentration is shown in Eq. 7:

$$F(D) = -4t/d \cdot t/dt \cdot (\phi_D/\phi) \qquad (7)$$

where ϕ_D is the cumulative volume fraction of a particle diameter below D.

When the particle sediments, the adjustment must be made for the sedimentation distance, s, as in Eq. 8, because s decreases with an increase in the sample meniscus in the manometer tube:

$$d(s-s_0)/dt = -d\log h/dt \cdot (R_m^2/R_s^2) \qquad (8)$$

where s_0 is the distance from the end of the capillary tube to the sample position at a hydrostatic balance in the sedimentation tube, as is shown in Fig. 1.

Experimental Results

Potato Starch Granule.—As an example of the sedimentation of dispersed particles, the potato starch granule was used, since it has such advantages as a large specific volume, a relatively spherical shape and a wide range of particle-size distribution.

The starch granule was extracted from fresh potatoes and then stored in a desiccator over calcium chloride until used. Suspensions of various concentrations were prepared with a 2 wt.% Tween 20 (polyoxyethylene sorbitan monolaurate) aqueous solution immediately before measurement.
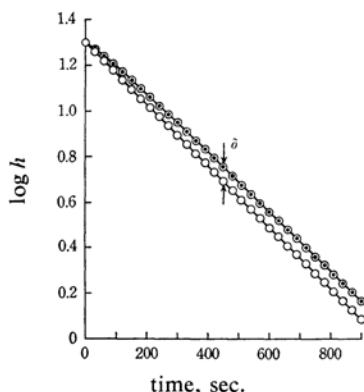
Fig. 4. Log h vs. time plots for 3.91 vol. % potato starch granule suspension (⊙) and its suspending fluid (○) at 32°C.

Figure 4 shows the plots of $\log h$ against time at 32°C for a 3.91 vol.% suspension and for a 2 wt.% Tween 20 aqueous solution. As may be seen in Fig. 4, these fluids do not show large differences of slopes from one another at the entire measuring times; hence, the d $\log h$/ dt procedure may not be directly applied with accuracy. To avoid this difficulty, the so-called "δ method"[1] was employed. That is to say, a straight line of the suspending fluid was assumed as the standard line; then the differences, δ, were measured between the curve of the suspension flow and the assumed line at the experimental values of t. When δ is plotted against t and the curve is differentiated at t, dδ/dt is obtained; from this quantity, d $\log h$/ dt is calculated.

Figure 5 gives the plots of $\log (m_0/m)$ against time deduced in this manner by using the data obtained from the relation between $\log h$ and t for a 2 wt.% Tween 20 aqueous solution and potato-starch-granule suspensions in various dispersion concentrations. Figure 6 shows the particle-size distribution of the potato starch granule, which was calculated from the decreasing curve in Fig. 5.
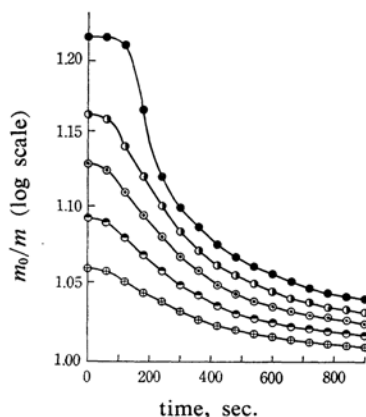
Fig. 5. m_0/m vs. time plots for potato starch granule suspensions of 5.75 vol. % (●), 4.84 vol. % (◑), 3.91 vol. % (⊙), 2.96 vol. % (◕) and 1.99 vol. % (⊕) at 32°C.
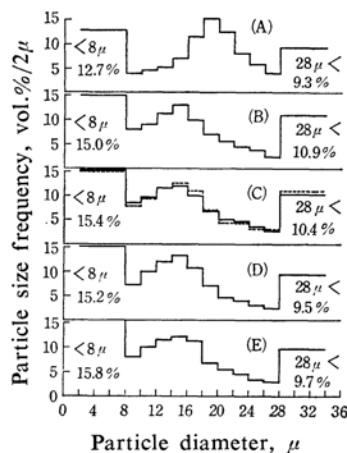
Fig. 6. Particle size distribution curves for potato starch granule suspensions of 5.75 vol. % (A), 4.84 vol.% (B), 3.91 vol.% (C), 2.96 vol.% (D) and 1.99 vol.% (E), calculated from m_0/m vs. time plots in Fig. 5. Broken line represents a result by using Wiegner's tube method.

The distribution curves differ slightly from each other in the shape but they all correspond to the maximum for the frequency, except for the suspension with a 5.75 vol.% concentration. From these results, it may be understood that the upper limit of the dispersion concentration for the determination is below about 5 vol.%. On the other hand, the lower limit of the dispersion concentration for the determination depends on the accuracy of viscosity measurement.

For the suspension of a 3.91 vol.% dispersion concentration, the result obtained by this method was compared with that obtained by Wiegner's

tube method,[4] which is shown as a broken line in Fig. 6.

Oil in Water Emulsions.—Emulsions of 1-hexanol, benzene or *n*-hexane in water, stabilized by 1 wt.% SDS (sodium dodecyl sulfate), were used for viscosity and particle-size determinations, as in the case of ascending particles.

These emulsions were readily prepared by shaking mixtures of the 9.1 vol.% oil phase and the residual water phase; the shakings were done under similar conditions so as to give products of the same dispersion state. However, the plots of log *h* against *t* for the emulsions differ according to the kind of dispersed liquids, as Fig. 7 shows. From these results, it is evident that the viscosity and the particle size of oil in a water emulsion are dependent on the nature of the dispersed substance, as Figs. 8 and 9 show. More detailed experi-
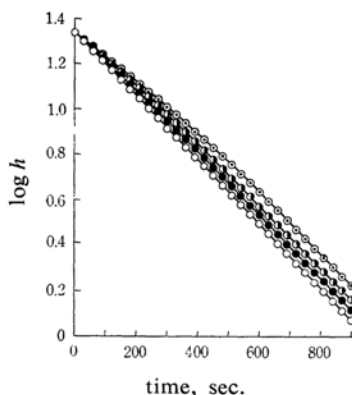

Fig. 9. Particle size distribution curves for emulsions of 1-hexanol (a), benzene (b) or *n*-hexane (c) in water.

mental results have been presented in a previous article.[5]

As for the application, the advantage of this method is that it enables one to obtain the viscosity of dispersions with quickly-sedimenting or -ascending particles. The viscosity appears in the initial slope of log *h* against the *t* curve where the original dispersion concentration is held.

Although independent of the particle size determination, the relation between the shearing stress and the rate of shear on the fluid may also be obtained from the measurements made during a single run,[1,6] so the apparatus can be used for the observation of the non-Newtonian flow.

Fig. 7. Log *h* vs. time plots for emulsions of 1-hexanol (☉), benzene (◖) or *n*-hexane (●) in water, stabilized by sodium dodecyl sulfate, and these spending fluid (○) at 32°C; dispersion concentration are 9.1 vol.% in all the systems.
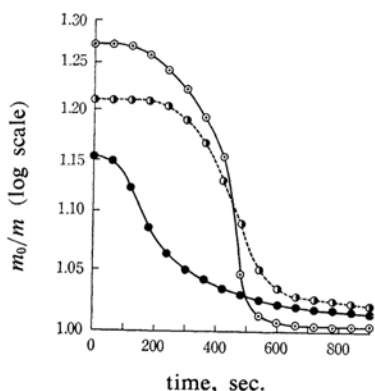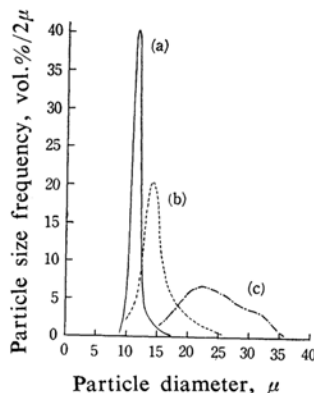
Summary

An apparatus for sedimentation analysis by the viscometric method, making possible the measurement of viscosity change with time at a fixed position in the bulk due to the sedimentation or ascension of dispersed particles, has be constructed. The new method has been examined with both a potato-starch-granule suspension and oil-in-water emulsions.

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Fig. 8. m_0/m vs. time plots for emulsions of 1-hexanol (☉), benzene (◖) or *n*-hexane (●) in water at 32°C.

4) W. Ostwald and F. V. Hahn, *Kolloid-Z.*, **30**, 26 (1922).

5) S. Matsumoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **85**, 741 (1964).
6) I. M. Kriger and S. H. Maron, *J. Appl. Phys.*, **25**, 72 (1955).