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Rheology of Concentrated Suspensions

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Synopsis

The dependence of the viscosities of highly concentrated suspensions on solids concentrations and particle size distributions is investigated by using an orifice viscometer. Based on the extensive amount of data on pertinent systems, an empirical equation which correlates the relative viscosities of suspensions (or relative moduli of filled polymeric materials) as a function of solids concentrations and particle size distributions is proposed. The equation has a constant which characterizes size distributions of spherical particles and can be determined experimentally without measuring viscosities. For uniform-size spherical particles, it reduces to the well-known Einstein equation at dilute solids concentrations.

INTRODUCTION

The rheological properties of concentrated suspensions are of interest in several applications. Manufacturing processes in which a large volume of concentrated suspensions is handled, such as the production of solid rocket propellents and of various filled polymeric materials, requires understanding and control of the basic rheological behavior of concentrated suspensions. The casting, mixing, and transfer of such materials generally require a knowledge of possible variation of viscosity with shearing rates as well as with concentration and particle size distribution. However, despite the importance of the problem, few experimental data exist for the effects of solids concentration and particle size distribution on the rheological properties of highly concentrated suspensions.

Much prior work in this field has been limited to relatively low solids concentrations. The viscosities of suspensions consisting of uniform-size rigid spherical particles were measured by Robinson,[1,2,14,15] Ting and Leubbers,[3] Vand,[4] Williams,[5] Sweeney and Geckler,[6] and Eveson.[7] The effects of particle size distributions on viscosities have been investigated by Roscoe,[8] Ward and Whitmore,[9] Sweeney,[10] and Eveson.[7] Although the average particle size in their works ranged approximately from 5 to 450 microns, the solids concentrations were mostly less than 50% by volume, and few existing data above 50% of solids show a significant disagreement.

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In this work, a specially designed viscometer is used to determine viscosities of highly concentrated suspensions near zero shear rates, and their dependence on solids concentrations and particle size distributions is investigated. The dependence of relative moduli of filled polymeric materials on solids concentrations and particle size distributions is also correlated with that of relative viscosity.

APPARATUS PERFORMANCE

The principal feature of the viscometer used to determine viscosities of concentrated suspensions near zero shear rate is based on the creeping flow of highly viscous fluid through a circular aperture. The details of the apparatus and a theory for the viscometer have been discussed elsewhere[11] and will not be repeated here. Instead, we discuss briefly the difference in performance between this viscometer and tube flow viscometers for concentrated suspensions.

The determination of the viscosity of a concentrated suspensions is complicated, since the flow field immediately adjacent to a surface, such

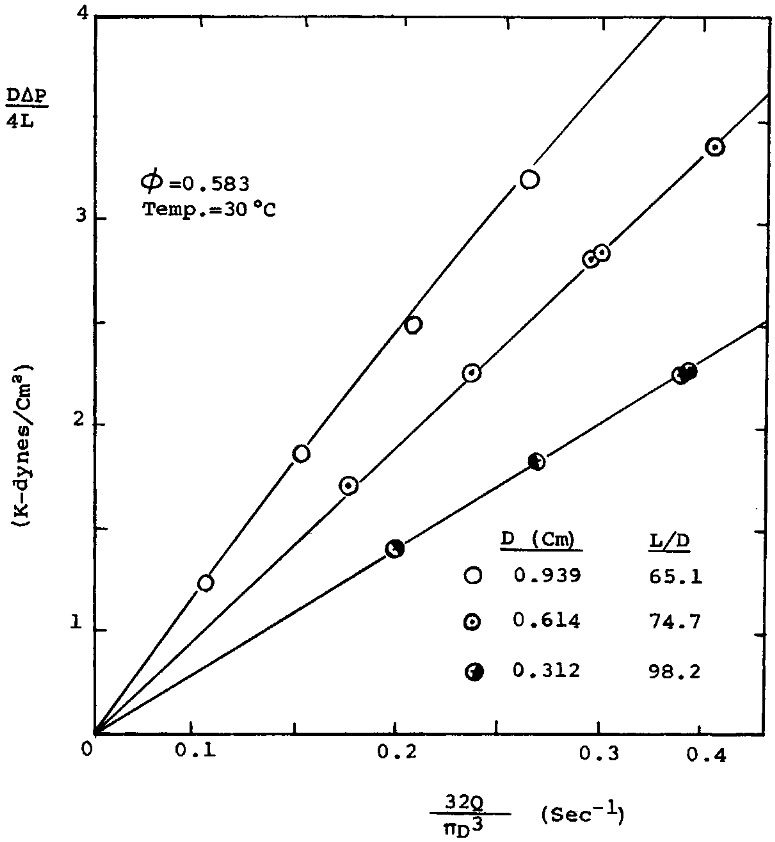


Fig. 1. Tube flow data of monodispersed system.

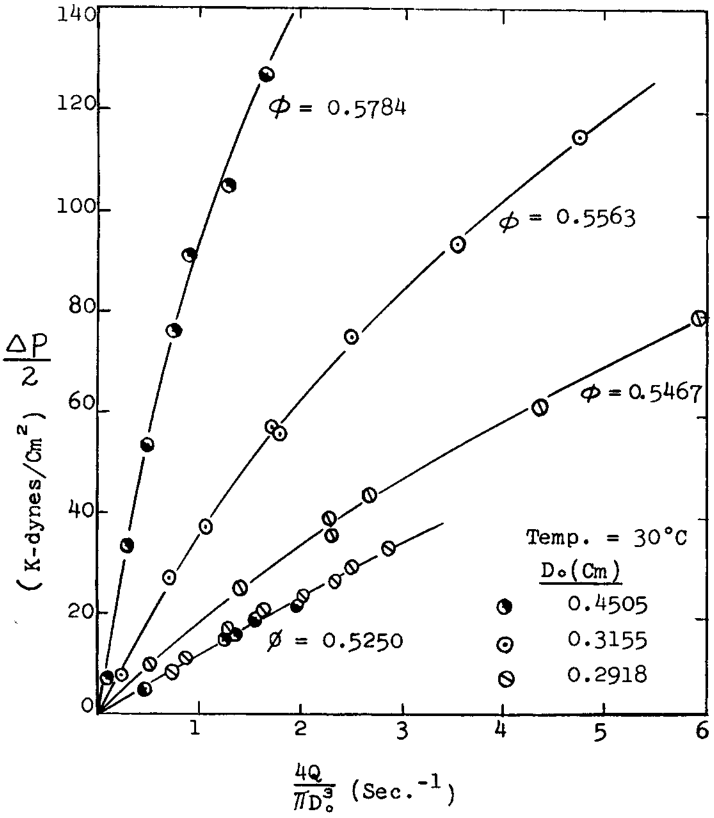


Fig. 2. Orifice viscometer data on monodispersed systems.

as the walls of a tube or of a Couette-type viscometer, is different from that in the bulk of the fluid. This is a consequence of the fact that particle migration away from the wall occurs in these viscometers. In cases where particles are so large that migration is important and concentration is so high that the major shearing occurs near the wall, most viscometers do not yield the data required for the accurate determination of suspension viscosity. We shall call this "wall effect."

This "wall effect" is most pronounced at high solids concentrations. For example, Figure 1 shows some experimental data obtained with a tube flow viscometer for a suspension of closely sized glass beads in a low molecular weight polyisobutylene (PIB). The PIB was found to exhibit Newtonian flow in the shear rate range studied, and its viscosity was about 20 poises at room temperature. The average diameter of the beads was about 50 microns, and the volume fraction of solids was 0.583. When plotted in this fashion, data for homogeneous fluids coincided for all tube diameters. However, a strong dependence of flow on tube diameter was noticed with concentrated suspensions. The performance of the sharp-edge orifice viscometer is shown in Figure 2. The figure shows that at very low shear rate, the suspension behaves like a Newtonian fluid. Furthermore, it has been found that the viscosities of these suspensions near zero shear rate are independent of the orifice diameter (e.g., $\phi = 0.525$ line in the figure). This fact at other solids concentrations will be discussed later in the correlation of viscosities.

EXPERIMENTAL

Concentrated suspensions were prepared using uniformly sized glass beads and the PIB as a suspension medium. The glass beads were produced by Minnesota Mining and Manufacturing Company. Particle size distribution was obtained from photomicrographs taken for each group of the sieved glass beads. The results are given in Tables I and II. Several typical photomicrographs are shown in Figure 3.

TABLE I
Particle Size Distribution of Glass Spheres
Used for Monodispersed Systems

Monodispersed system	Size range, microns	%	Specific gravity	D_{vs}[a]
M-1	80–70	86.7	2.418	73.8
	69–60	13.3		
M-2	125–110	97.1	2.418	112.5
	109–100	2.9		
M-3	61–55	28.27	2.253	53.8
	54–50	59.38		
	49–43	12.35		
M-4	250–234	55.07	2.475	236.0
	233–220	33.34		
	219–210	11.59		
Smallest size glass beads used for bimodal systems	50–40	2.5	2.294[b]	33.0
	39–30	58.7		
	29–25	38.8		

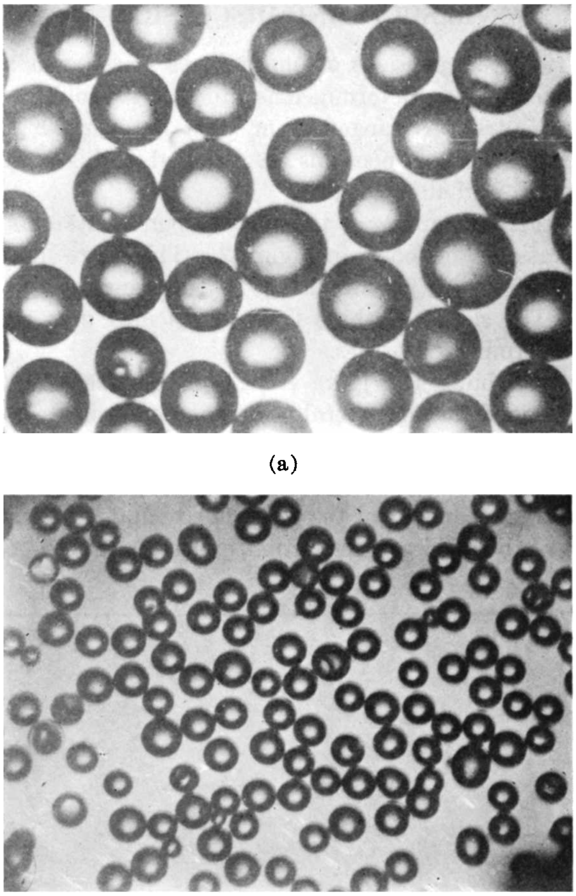
[a] Volume-surface mean diameter.

[b] Large number of gas bubbles in glass beads.

TABLE II
Particle Size Distribution of Glass Spheres
Used for Bidispersed Systems

Bidispersed system	Distribution		Specific gravity[a]	Diameter ratio
	Large spheres	Small spheres		
B-1	same as M-4	smallest size	2.434	0.138
B-2	same as M-4	same as M-1	2.463	0.339
B-3	same as M-4	same ad M-2	2.463	0.477

[a] Calculated based on the bimodal composition.



(a)

(b)

Fig. 3. Sieved glass beads used for suspensions. (a) Volume surface mean diameter; $D_{vs} = 235.0$ microns. (b) Volume-surface mean diameter; 112.5 microns.

The glass beads were dried in a vacuum oven at 110°C for several hours, mixed with PIB under vacuum (approximately 0.1 in. of Hg). The mixer had two horizontal finger-type mixing braids and was jacketed with cooling water at a constant temperature. Usually 2 or 3 hr of mixing was sufficient to remove finely dispersed air bubbles. Following this, the concentration of suspension was determined for two samples taken from different positions in the mixer. Any entrapped air introduced during transfer of the suspension into the viscometer was removed by subjecting the mixture in the viscometer to a deaerating suction hood mounted on top of the viscometer barrel. Runs were made by applying constant gas pressure on the viscometer barrel and measuring steady-state flow rate.

Although the corrections for the hydrostatic heads were small in comparison with the applied gas pressure, they were added to the total pressure drops.

RESULTS AND DISCUSSION

The viscosities of suspensions of uniform-size glass beads ranging from 53.8 to 236.0 microns were determined as a function of solids concentration. The solids concentrations ranged from 45% to over 60% by volume. The viscosities of all the suspensions investigated in this work were determined at 20°, 30°, and 40° ± 0.1°C.

Several typical flow curves of the monodispersed systems at different solids concentrations are shown in Figure 2. The figure shows that these suspensions behave like pseudoplastic in the range of shearing rates investigated. The slopes of these flow curves near zero shear rate are measured to determine viscosities.

The results are shown in Figure 4. Despite the fact that these data have been obtained using several different-size orifices ranging from 0.216 to 0.403 cm in diameter, within the experimental errors they are independent of the orifice size. For the monodispersed systems, the relative viscosity is independent of the particle size and temperature and is a function only of the solids concentration. The relative viscosity tends to

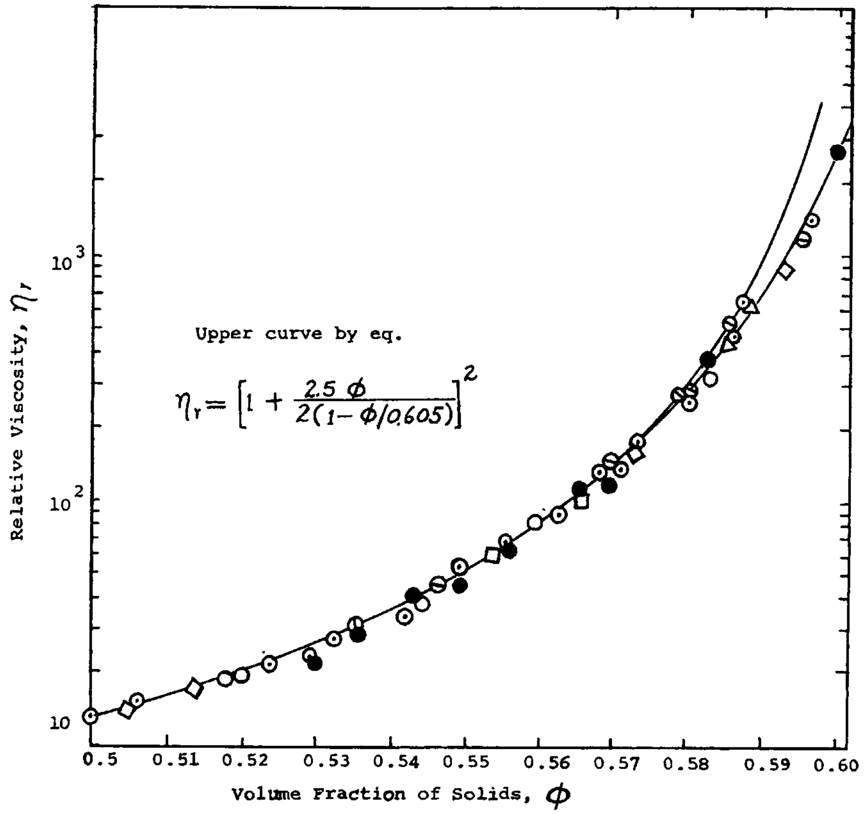


Fig. 4. Viscosity of monodispersed systems and comparison of equations.

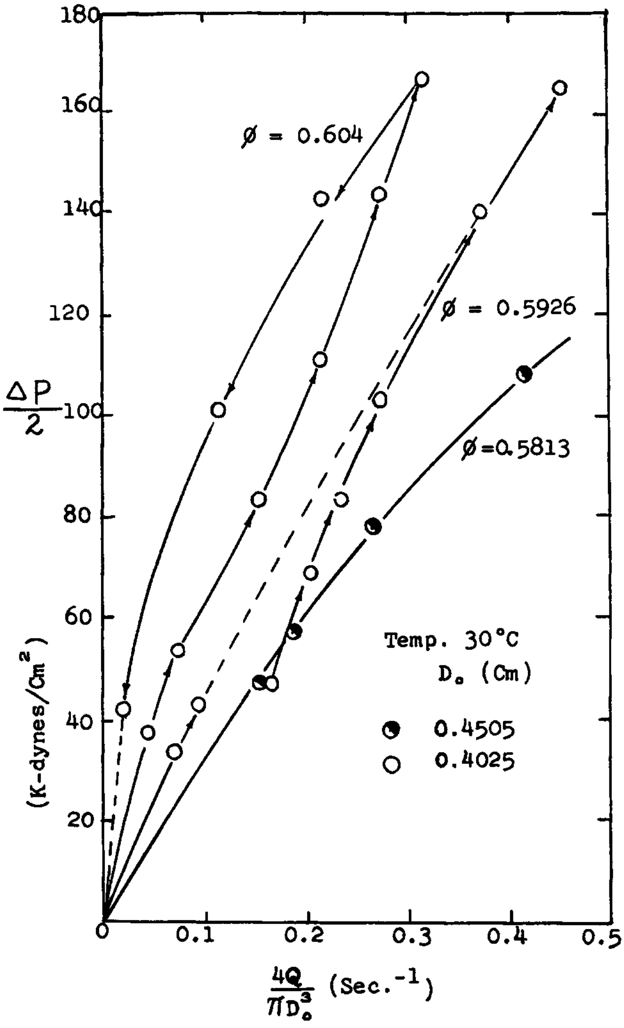


Fig. 5. Anomalous flow behavior of monodispersed systems.

approach infinity asymptotically to 60.5% by volume of solids. At a concentration of about 50%, a rather rapid increase in viscosity is particularly noticeable. This is expected because the loose-packed condition for a random bed of uniform spheres corresponds to 52% by volume,[12,13] and at this concentration the friction due to particle interaction would become a significant factor, and its resistance to shear seems to cause the rapid increase in viscosity.

At a concentration near 60% by volume of solids, the flow behavior of monodispersed systems shows peculiar hysteresis behavior. Figure 5 shows these behaviors at several solids concentrations. It is evident that the hysteresis behavior is different from the usual thixotropy. This peculiar flow behavior is believed to be caused by volumetric dilatancy at high solids loading.

The temperature dependence of viscosities of monodispersed as well as bidispersed systems was also investigated. For a given solids concentration, Arrhenius-type of plotting of viscosity versus temperature yielded a straight line parallel to PIB at zero solids concentration. This indicated that the activation energy for the viscous flow was not affected by the solids particles.

The solids concentration for monodispersed systems at which the relative viscosity tends to become infinite has been a subject of much study. Eilers[14] measured viscosities of concentrated bitumen suspensions with a tube flow viscometer and found that the solids concentration ϕ was approximately 0.74 corresponding to a rhombohedral packing. Ting and Luebbers[3] used a Brookfield viscometer to measure viscosities of suspensions of sized glass beads and found that the maximum solids concentration was approximately 0.52 corresponding to a cubic packing. Maron and Krieger[15] investigated both synthetic and natural latices emulsion-suspensions and reported several different values for the maximum solids concentration. For the case of natural latex suspensions, ϕ_∞ was approximately 0.74, indicating the densest packing of spheres. However, in the case of Neoprene latex, it ranged from 0.55 to 0.61, indicating any type of packing between cubic and orthorhombic. It appears that the disagreement among the reported ϕ_∞ may be caused partly by particle size variation, since much of the reported data were not obtained with truly monodispersed systems. The disagreement among the reported data could also have been effected by particle rigidity. The so-called wallslip may become a significant factor in determining the maximum solids concentration. The results of this investigation with uniform-size glass beads show that ϕ_∞ is about 0.605, indicating an orthorhomic type of packing and is independent of the particle size. Above this concentration, suspensions show hysteresis behavior even at low shear rates.

Bidispersed Systems

The effects of particle size distributions on viscosities were investigated using several different bidispersed systems. The total solids concentrations ranged from 54% to 74% by volume. The particle size ratios were chosen to permit packing of small spheres into the interstices between large spheres. The large-size glass beads used in this work had a volume-surface mean diameter at 236.0 microns, the small spheres, a volume-surface mean diameter of 112.5, 73.8, and 33.0 microns. This led to a diameter ratio of small to large spheres of 0.477, 0.33, and 0.138, respectively. The diameters of small spheres have been chosen so that 112.5-micron spheres are too large to fit into square holes created by large spheres, while 33.0-micron spheres could easily thread through the labyrinth of large spheres.

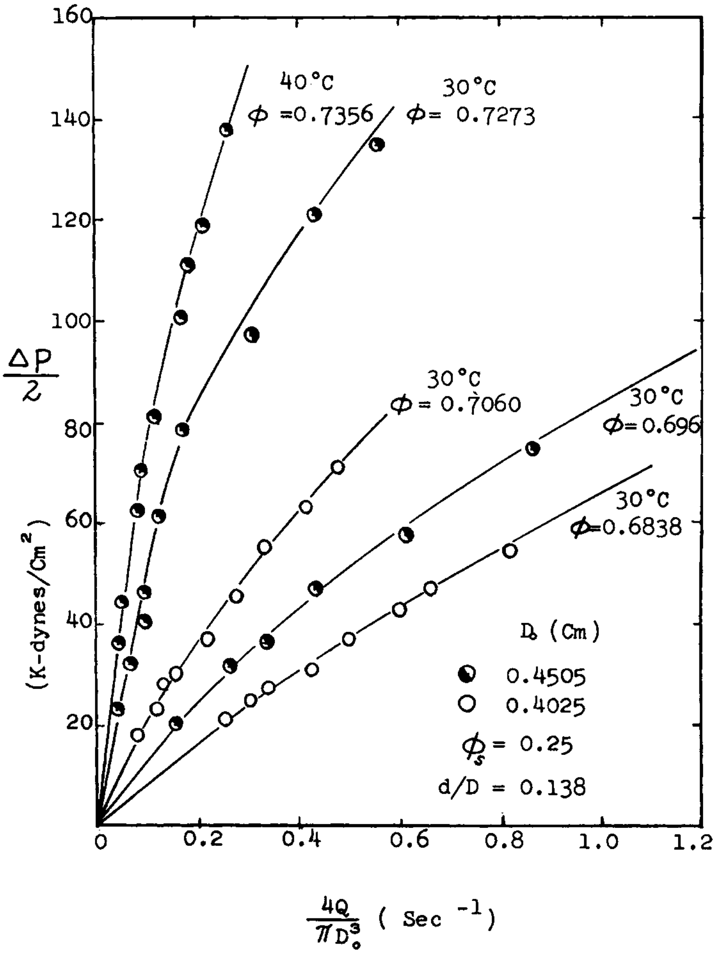


Fig. 6. Orifice viscometer flow curves of bimodal systems.

Geometric considerations on the packing of two different-size spheres show that the relative amount of large and small spheres is important if a high solids loading is to be achieved. In this study, each bimodal suspension had 25% by volume of the total solids as small spheres. Several typical flow curves of bimodal suspensions are shown in Figure 6. It is interesting to note that these data were obtained at much higher solids concentrations than those of the monodispersed systems which exhibited hysteresis. No hysteresis flow behavior was observed with bimodal suspensions investigated in this work. Figure 7 shows the viscosities of several bimodal suspensions as a function of solids concentration at several particle size ratios. It is seen from the figure that the relative viscosity decreases markedly as the particle size ratio decreases. This indicates that the solids concentration in a suspension can be increased significantly while maintaining a desired viscosity.

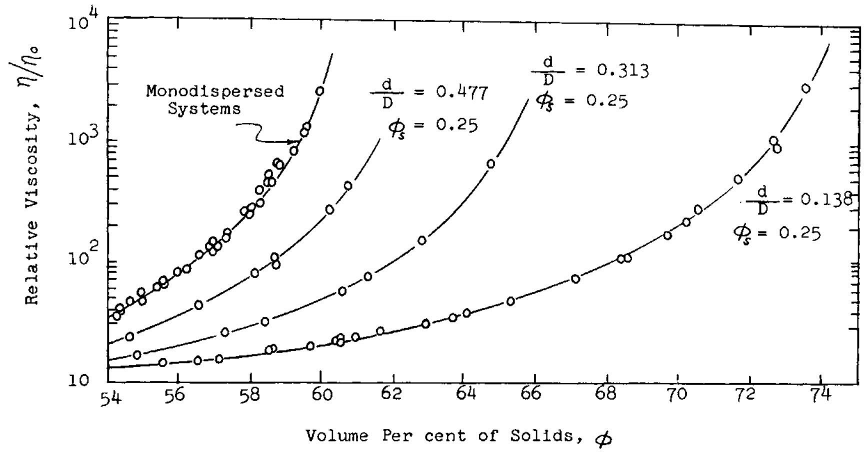


Fig. 7. Dependence of relative viscosities on solids concentrations and particle size distributions.

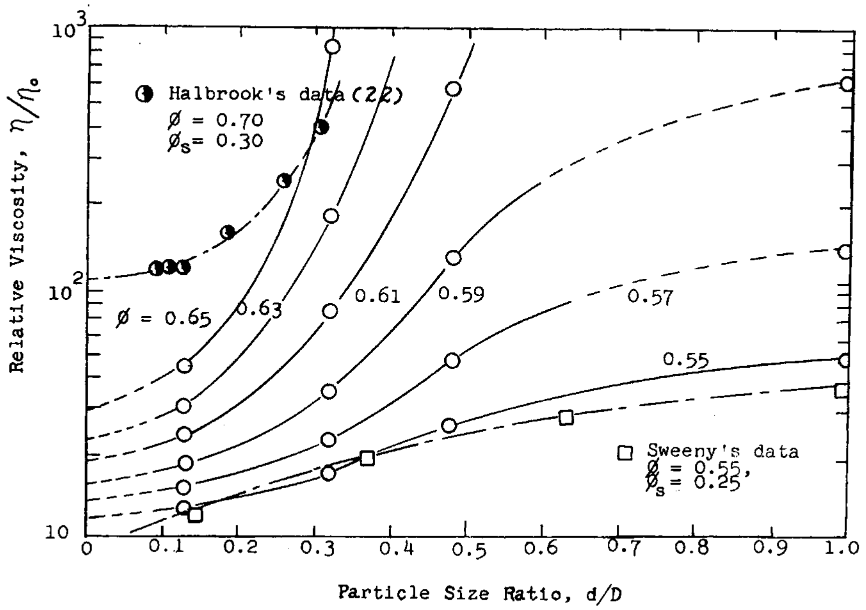


Fig. 8. Particle size distribution effects on viscosities of bimodal suspensions.

The dependence of the relative viscosities of bimodal suspensions on particle size ratios at a given total solids loading is shown in Figure 8. For comparison, Sweeney's rotational viscometer (Couette flow) data are shown in the figure. Inspection of the figure shows that at a given total solids loading, there is a particle size ratio below which the relative viscosity does not decrease in any appreciable amount. The limiting particle size ratio of small to large spheres is about 1/10, and at this size ratio the small spheres could be threaded easily through a labyrinth of large spheres.

Along a constant ϕ-line in the figure, as the particle size ratio decreases, the number of small spheres increases. Since all bimodal suspensions investigated in this work had 25% small spheres in total solid phase, the number of small spheres per a large sphere, which is independent of the total solids concentration, can be calculated easily. For example, at a size ratio of 1/10, this number is about 333, while at a size ratio of 1/2, it is only about 2.67. The fact that the relative viscosities of bimodal suspensions decreases significantly as the number of small spheres increases seems to indicate that the fine spheres act like ball bearings between large spheres. However, if the particle size ratio is less than 1/10, this action appears to cease gradually and the small spheres seem to behave essentially like a fluid toward the larger spheres. This behavior was also observed in sedimentation of a large sphere in suspensions of small spheres.[16]

Correlation of Viscosity and Modulus

No satisfactory theoretical or empirical equation exists to predict viscosities of suspensions for wide ranges in solids concentrations and particle size distributions.

The viscosities of monodispersed systems investigated in this work as well as the published data at lower solids concentrations are shown in

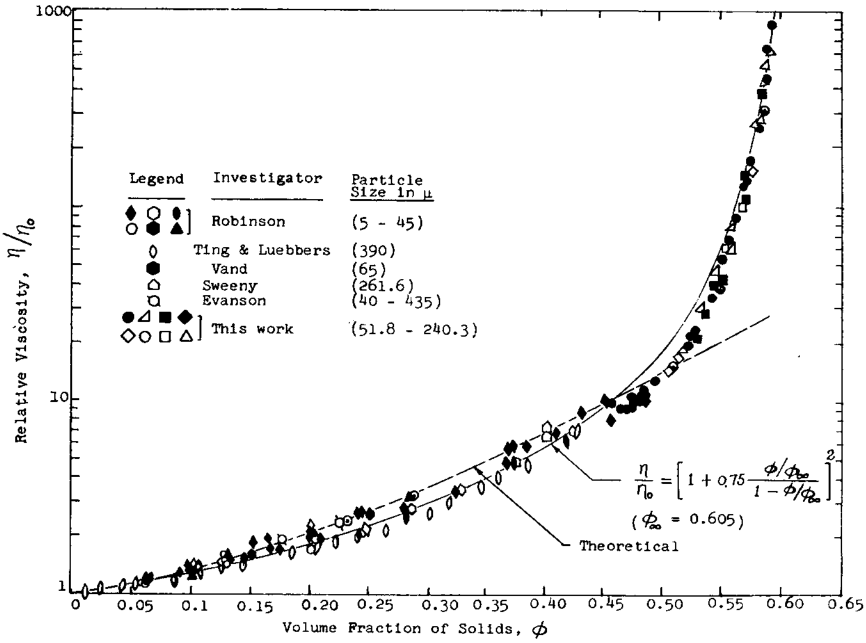


Fig. 9. Relative viscosities of monodispersed systems.

Figure 9. The figure shows that the orifice viscometer data near 45% solids are in good agreement with those obtained by other investigators who used Couette-type viscometers.[1,2,5,6] However, viscosities measured with a Brookfield viscometer[3] and a tube flow viscometer[14] are slightly lower than those obtained with a rotational viscometer. The solid line in the figure represents an empirical equation of the type proposed by Eilers with a different constant. The dotted line represents a theoretical equation obtained in this work. The details of the theory will be published in the near future.

In correlating the relative viscosities as a function of solids concentration and of particle size distributions, the maximum solids concentration, ϕ_∞, to which the relative viscosity approaches infinity asymptotically has to be introduced in the correlation. Although measurement of the actual viscosity at ϕ_∞ is not possible, it can be determined by plotting $\phi\eta_r/(\eta_r - 1)$ versus ϕ and extrapolating the straight line to a point where the two variables become equal. Figure 10 shows several examples of such plots.

We find that if the relative viscosities of monodispersed as well as bidispersed systems are plotted as a function of the reduced solids volume defined as ϕ/ϕ_∞, all the data obtained in this work fall on a single curve. This indicates that such a correlation may be valid even for less concentrated suspensions. Available data in the literature for pertinent systems

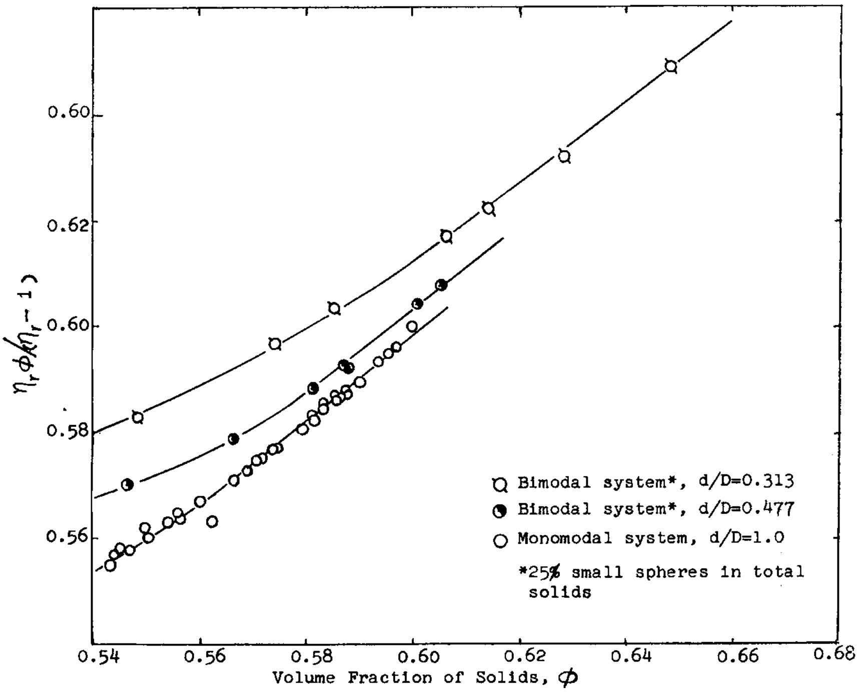


Fig. 10. Graphical evaluation of maximum solids concentrations.

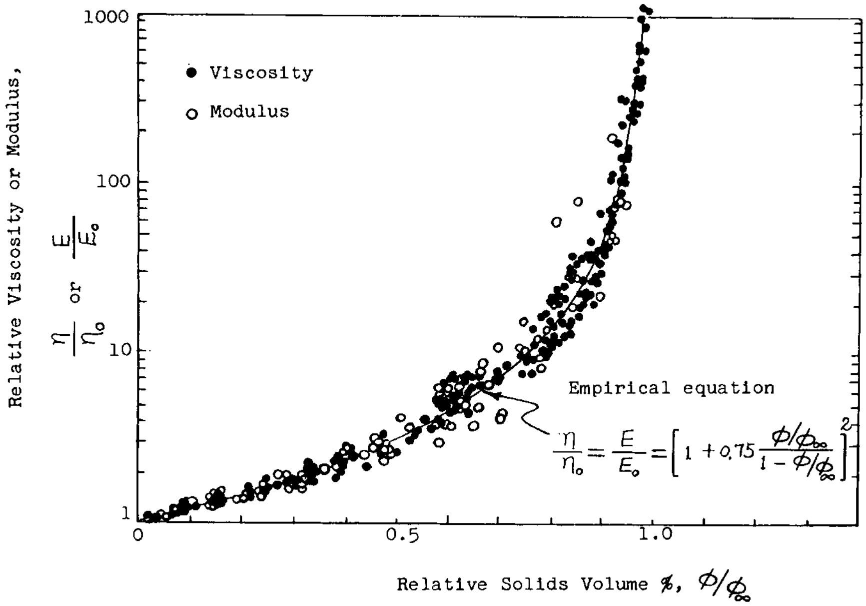


Fig. 11. Dependence of relative viscosity or modulus on solids concentrations.

have been collected to investigate the validity of the correlation. Figure 11 shows a master curve obtained with the data from many different sources.[1–3,10,17–22] These data include viscosities of many different suspensions as well as moduli of crosslinked and amorphous viscoelastic materials filled with spherical particles of various sizes and size distributions. The solid line in the figure is represented by the following equation:

$$\frac{\eta}{\eta_0} = \frac{E}{E_0} = \left[1 + 0.75\left(\frac{\phi/\phi_\infty}{1 - \phi/\phi_\infty}\right)\right]^2 \qquad (1)$$

where E is Young's modulus and zero subscript denotes no solid loading. It should be pointed out that practically all the viscosity data for ϕ/ϕ_∞ greater than 0.75 were obtained in this work. Despite the fact that the data shown in the figure have been obtained by different experimental methods using various systems, the agreement between relative viscosity and relative modulus as a function of the reduced volume concentration seems to be remarkably good. The correlation indicates that the relative viscosity of suspensions of spherical particles is independent of particle size and of particle size distribution and is only a function of the reduced volume concentration. If the maximum solids concentration, ϕ_∞, for the monodispersed suspensions is taken to be equal to 0.605, eq. (1) reduces to the well-known Einstein equation at dilute concentrations. It is obvious from the correlation that the relative viscosity and the relative modulus can be predicted if the maximum solids concentration is known as a function of particle size distribution.

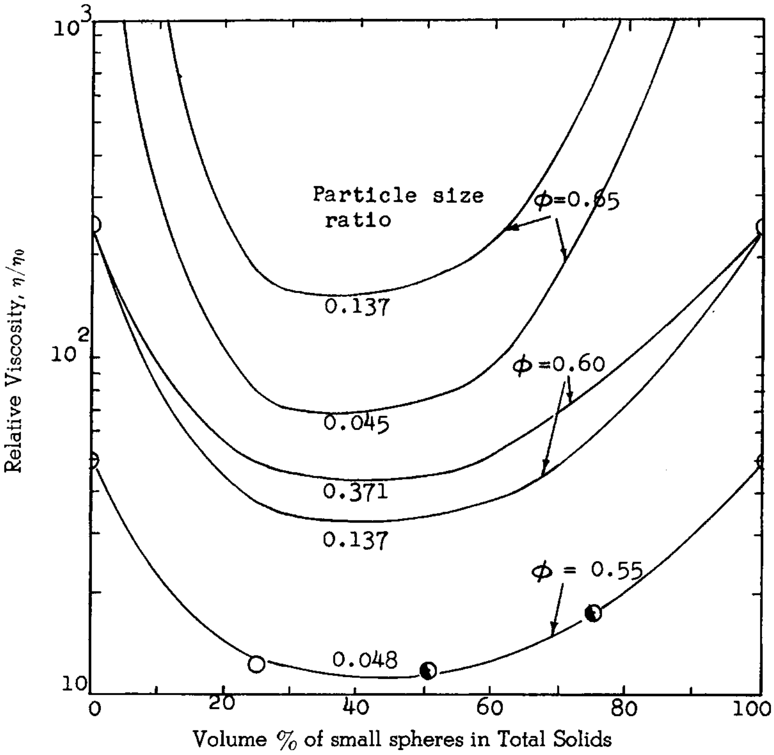


Fig. 12. Calculated viscosities or moduli at various particle size distributions. (○) this work; (◐) Sweeny's data.

Sweeny calculated volume per cent of voids in several bimodal suspensions by measuring bulk densities. From these data, the maximum solids concentration can be calculated as a function of the particle size ratio and of composition of bimodal suspensions. Based on ϕ_∞ obtained by Sweeny and using eq. (1), the variation of the relative viscosities or moduli as a function of suspension compositions has been calculated at several total solids concentrations. The results are shown in Figure 12. It is interesting to note in the figure that at a given total solids concentration there are regions where a small change in suspension composition causes a large variation in viscosity or modulus of highly loaded systems, while in the other region even relatively large changes in composition cause little variation.

CONCLUSIONS

The relative viscosities of monodispersed systems investigated in this work are independent of the particle size and temperature and are a function only of solids concentrations.

Above 50 vol-% solids, the viscosity of monodispersed systems increases much more rapidly with increase in solids concentrations than at the less concentrated range. It was not possible to observe this effect by using conventional viscometers. The viscosities of monodispersed systems all tend to approach infinite asymtotically to $\phi = 0.605$.

Based on the extensive amount of data, an equation which correlates relative viscosities as well as relative moduli as a function of solids concentration and particle size distribution is proposed. For uniform-size spherical particles at dilute concentrations, this equation reduces to Einstein's equation. The equation predicts compositions of bimodal systems which would give minimum viscosity at a given total solids concentrations. The minimum viscosity or modulus of a bimodal system can be achieved with 25% to 35% of solids as fine spheres, the remainder being the coarse size. This is in agreement with experimental data obtained by other investigators at moderate solids concentrations.

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