

period of τ_2 and then returned to zero. This implied that no appreciable ionic exchange took place between albumin and the exchanger.

The results shown in Figure 11 illustrate the importance of selecting the appropriate pH levels for the parapumping separation. Consider a solution of n proteins ordered according to their isoelectric point, I_i . Choose two pH values P_1 and P_2 such that

$$I_1 < I_2 < \dots < I_m < P_2 < I_{m+1} < \dots$$

$$< I_{n-1} < I_n < P_1$$

The first m components will bear a negative charge, whereas the others will carry a negative charge at P_1 and a positive charge at P_2 . Therefore, the latter group will be bound to a suitable cationic exchanger at P_2 and released at P_1 , while the first m components will be unaffected. Thus, a parametric pump operating with levels of P_1 and P_2 should be capable of removing the components $m + 1, \dots, n$ from one product stream and enriching the other product stream with these components.

Many versions of parametric pumps are conceivable. The pump examined here appears to be a very promising device for separating two or multicomponent protein mixtures.

ACKNOWLEDGMENT

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NOTATION

- I_i = isoelectric point for component i
 n = number of cycles of pump
 P_1 = high pH
 P_2 = low pH
 Q = reservoir displacement rate, cm^3/s
 Qt_i = upflow displacement, cm^3

- Qt_{II} = volume of top product, cm^3
 Qt_{III} = downflow displacement, cm^3
 Qt_{IV} = volume of bottom product, cm^3
 t_I = duration of downflow, s
 t_{II} = duration of bottom feed, s
 t_{III} = duration of upflow, s
 t_{IV} = duration of top feed, s
 V_B = bottom reservoir dead volume, cm^3
 V_e = void volume, cm^3
 V_T = top reservoir dead volume, cm^3
 W = weight fraction of solute based on total weight of proteins, (kg/kg)
 $\langle W_P \rangle_n$ = average W in the product at n^{th} cycle, (kg/kg)
 $\langle W_{BP} \rangle_n$ = average W in the bottom product at n^{th} cycle, (kg/kg)
 $\langle W_{TP} \rangle_n$ = average W in the top product at n^{th} cycle, (kg/kg)
 y_0 = concentration of solute in the feed, kg moles/ cm^3
 $\langle y_{BP} \rangle_n$ = average concentration of solute in the bottom product at n^{th} cycle, kg moles/ cm^3
 $\langle y_{TP} \rangle_n$ = average concentration of solute in the top product at n^{th} cycle, kg moles/ cm^3

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Rheological Characteristics of Solid-Liquid Mixtures

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The relationship between the shear stress and strain rate of a mixture consisting of solid particles suspended in a Newtonian fluid depends upon the physical properties of the mixture as well as kinematic features of the flow. Functional relationships for rheological properties of mixtures are derived and compared to measured results obtained by previous investigators.

SCOPE

The design of a system to transport a suspension of solids in a fluid medium requires knowledge of the constitutive equations of the mixture. A theoretical description of these equations are presented for mixtures where only mechanical and hydrodynamic effects are significant. The two-component mixture under consideration consists of rigid spherical particles suspended in a Newtonian fluid.

The mixture, however, can not, in general, be considered as having Newtonian properties. Two flow regimes for a solid-liquid mixture are described, one of which does exhibit Newtonian characteristics with the other region having a nonlinear relationship between shear stress and strain rate. The theoretical analysis describing the constitutive relationships in the Newtonian range are compared to experimental results obtained by previous investigators. The analytical developments are shown to be valid for a large range of concentrations of solids.

CONCLUSIONS AND SIGNIFICANCE

In addition to effects produced by thermal, electrical, and van der Waal forces, the constitutive equations of a solid-fluid mixture have been considered by previous investigators to be dependent upon, among other factors, the kinematic features of the flowing mixture. The results of this investigation consider only mechanical and hydrodynamic effects on the flow of a mixture containing rigid, spherical particles and identify two flow regimes: one in which the shear stress in a mixture is proportional to the strain rate and another which non-Newtonian characteristics are exhibited. A parameter indicating the relative magnitude of inertia and viscous forces is used to differentiate the regions where the mixture exhibits Newtonian and non-Newtonian properties.

Constitutive equations have been developed for both the Newtonian and non-Newtonian types of flows. In the Newtonian region, equations relating the shear stress and strain rate are shown to be proportional to a function which is dependent upon the concentration of solids within the mixture and the viscosity of the fluid in which the solids are suspended. The theoretically determined relationship is compared to the experimental results of previous investigators and is found to be in good agreement. In the non-Newtonian flow region, the shear stress is shown to depend upon the density and concentration of the solid and liquid portions of the mixture, the particle geometry, and the velocity gradient of the mixture.

BACKGROUND

One of the most frequently quoted references on the behavior of solid-liquid mixtures is the classical analysis of Einstein (1956). Considering solely hydrodynamic effects, Einstein determined theoretically that a solid-liquid mixture of low concentration behaved as a Newtonian fluid. As shown in Equation (1), the effective viscosity μ^* of such a mixture, as determined by Einstein, is a function of the volume concentration ϕ of solid particles and the viscosity of the fluid portion of the mixture:

$$\mu^* = \mu_0(1 + 2.5\phi) \quad (1)$$

Many subsequent investigators developed equations similar to Equation (1) employing fewer restrictive assumptions in their derivation. These equations were generally of the form

$$\frac{\mu^*}{\mu_0} = \mu_r(\phi) \quad (2)$$

A common feature to these theoretically derived relationships is that the increased viscosity of the mixture is looked upon as a consequence of the perturbation of the flow field around particles suspended in the moving fluid.

Based on methods commonly used in lubrication theory, an asymptotic analytical expression was derived by Frankel and Acrivos (1967) for the effective viscosity of

mixtures in highly concentrated suspensions of solid spheres. Considering only the effects of hydrodynamic interactions among particles in relative motion and in close proximity to one another, their analysis showed a good agreement with experimental results obtained by Rutgers (1962) and Thomas (1965) for concentrations greater than 0.5. Inertia effects were considered to be negligible in these studies.

Jeffrey and Acrivos (1976) reviewed experimental and theoretical work on the rheological properties of suspensions of rigid particles. The assumption that an effective viscosity depending solely on the volume fraction of the particles suffices to describe the rheology of suspensions was shown to be inadequate. The cause of non-Newtonian behavior of mixtures was attributed largely to the effects of various nonhydrodynamic forces common to contiguous solids of extremely small particle size.

THEORY: VISCOUS DOMINATED REGION

Consider the two-dimensional motion of a solid-liquid mixture described by the velocity field $u(y)$, where u is the velocity component of the mixture in the x coordinate direction. Assume also that the solid particles forming the mixture are spheres and that their representative particle orientation is given by the cubic packing shown in Figure 1a. The velocity profile $u(y)$ representing the averaged motion of the mixture can be described by the linear relationship shown by the dashed line in Figure 1b. The profile $u(y)$ can be considered as the macroscopic description of the flow of the mixture.

The velocity profile considered to represent separately the motion of the individual solid and fluid components of the mixture is referred to as the microscopic description of the flow. The model used to represent the microscopic description of the mixture kinematics considers that the velocity of a solid particle is equal to the velocity $u(y)$ evaluated at the position of the center of the spherical particle as shown in Figure 1b. No slip conditions are considered at the solid-liquid interfaces. Linear variations in velocity are assumed within the fluid portion of the mixture. Throughout the x - z plane containing point A, which forms the upper boundary of the cubic packing shown in Figure 1a, the velocity of the solid and fluid elements are considered to be everywhere identical. Similarly, the solid and fluid elements on the x - z plane containing point B are

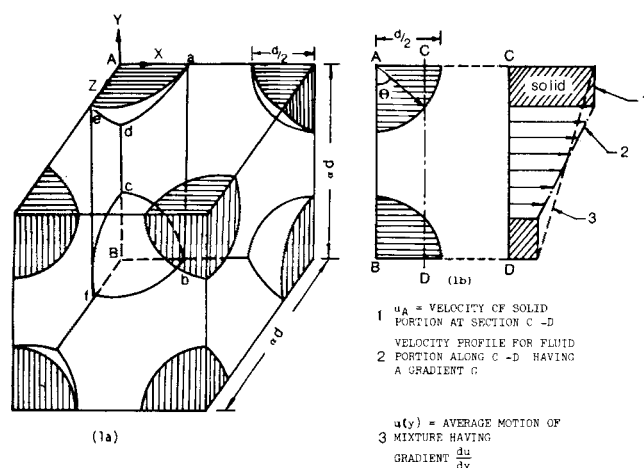


Fig. 1. Orientation of particles in viscous dominated region.

considered to have identical velocities. Both the microscopic and macroscopic descriptions of the kinematics of the mixture produce identical mass rates of flow for the movement of the solid and fluid elements in Figure 1a. Hence, the microscopic description of the movement of the solid and liquid components of the mixture is an admissible model from considerations of mass conservation.

The effective viscosity of the mixture is obtained by determining the viscous dissipation produced by the fluid within the volume $(\alpha d)^3$ bounding the cubic packing shown in Figure 1a. Inside the surface (a-b-c-d) the local velocity gradient G , at $Z = 0$, and $0 \leq x \leq d/2$ can be described as

$$G = \frac{\alpha d \frac{du}{dy}}{d(\alpha - \cos\theta)} \quad \text{for} \quad \begin{cases} 0 \leq x \leq \frac{d}{2} \\ z = 0 \end{cases} \quad (3)$$

The average of the square of the gradient G at $Z = 0$ between $x = 0$ and $x = 0.5d$ hence becomes

$$\begin{aligned} \overline{G^2} &= \int_0^{\pi/2} \left[\frac{\alpha \frac{du}{dy}}{\alpha - \cos\theta} \right]^2 \cos\theta d\theta \quad \text{for } 0 \leq x \leq 0.5d, Z = 0 \\ \overline{G^2} &= \left(\alpha \frac{du}{dy} \right)^2 \left(\frac{1}{\alpha^2 - 1} \right) \left(1 + \frac{2}{\sqrt{\alpha^2 - 1}} \tan^{-1} \sqrt{\frac{\alpha + 1}{\alpha - 1}} \right) \quad (4) \end{aligned}$$

The value $\overline{G^2}$ will be considered to represent the average value of the square of the velocity gradient at all positions within the fluid volume contained within the surface (a-b-c-d-e-f). This approximation overestimates the viscous dissipation of the fluid bounded by that surface. This overestimation becomes pronounced at large concentrations and may be one of the reasons why Equation (7) overestimates the energy dissipation at concentrations greater than 0.5 as shown in Figure 2. The fluid not contained in the four fluid columns similar to (a-b-c-d-e-f) has a local velocity gradient everywhere equal to du/dy . Therefore, throughout the four regions similar to (a-b-c-d-e-f), having a total volume $V_1 = d^3(\pi/4 \alpha - \pi/6)$, the average of the gradient squared is considered to be $\overline{G^2}$ as described by Equation (4), while in the remaining volume $V_2 = (d^3 d^3 - \pi/4 \alpha d^3)$, the gradient squared is $(du/dy)^2$.

Equating the rate of viscous dissipation of energy to the rate with which work is performed by the force F required to displace the top row of particles in Figure 1 relative to the lower row, we get

$$F \frac{du}{dy} \alpha d = \mu_o \int_{V_1} \overline{G^2} dV + \mu_o \int_{V_2} \left(\frac{du}{dy} \right)^2 dV \quad (5)$$

In Equation (5), the viscous dissipation is considered to occur throughout the volume $V = (\alpha d)^3 (1 - \phi)$, and μ_o is the viscosity of the fluid portion of the mixture.

If we define F as the shear stress τ_μ multiplied by the area $(\alpha d)^2$, Equation (5) becomes

$$\tau_\mu = \mu_o \mu_r \frac{du}{dy} \quad (6)$$

where

$$\mu_r = \left(1 - \frac{\pi}{4\alpha^2} \right) + \left(\frac{\pi}{4} - \frac{\pi}{6\alpha} \right) \left(\frac{1}{\alpha^2 - 1} \right)$$

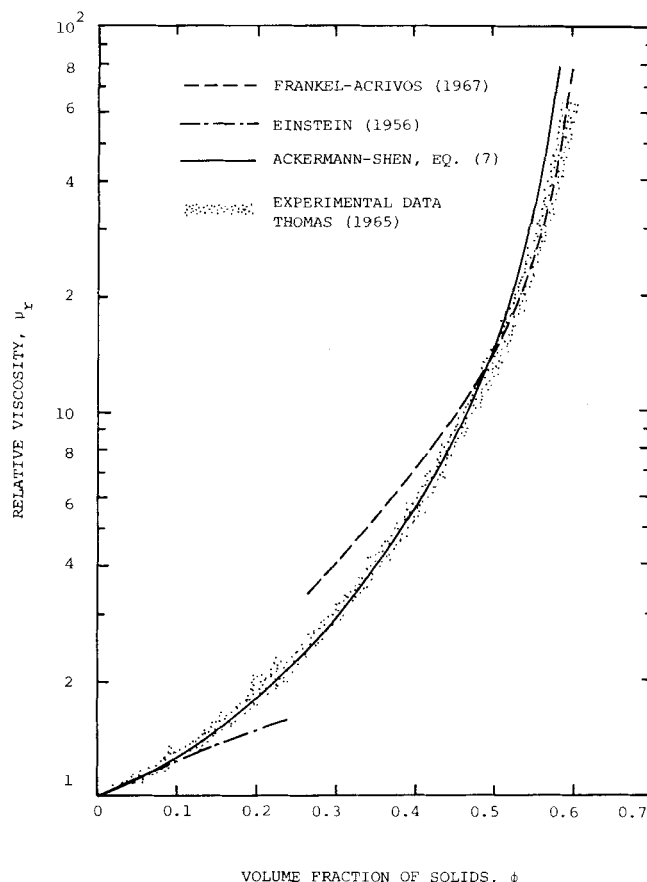


Fig. 2. Theoretical and experimentally determined relationships between relative viscosity and volume concentration of solids.

$$\left(1 + \frac{2}{\sqrt{\alpha^2 - 1}} \tan^{-1} \sqrt{\frac{\alpha + 1}{\alpha - 1}} \right) \quad (7)$$

From geometric considerations, the parameter α can be expressed in terms of a reference concentration ϕ_* using Equation (8):

$$\alpha = \left(\frac{\phi_*}{\phi} \right)^{1/3} \quad (8)$$

Equation (7) indicates that a solid-liquid suspension can be considered as a Newtonian fluid provided that the shear stresses are produced solely as a result of viscous dissipation within the fluid caused by the relative motion of adjacent solid particles.

COMPARISON WITH EXPERIMENTAL RESULTS

Many experimental studies exhibiting a wide scatter in data have been carried out to determine a suitable form for Equation (2). Rutgers (1962) summarized many of these studies and obtained an average curve. Thomas (1965) showed that the scatter common to available experimental information can be reduced by using extrapolating procedures to eliminate or minimize the colloid-chemical, inertia, and nonhomogeneous effects. Figure 2 shows the comparison of this reduced data to results predicted using Equation (7). The value of $\phi_* = 0.625$ was used to determine α in Equation (7) since 0.625 represented the value of ϕ_* used by Thomas. It is of interest that 0.63 is equal to the average of the ϕ_* values for a cubic (least dense) and rhombohedral (most dense) packing. In the movement of solid-liquid mixtures, it is reasonable to assume that the ϕ_* value representative of the changing orientation of the particles

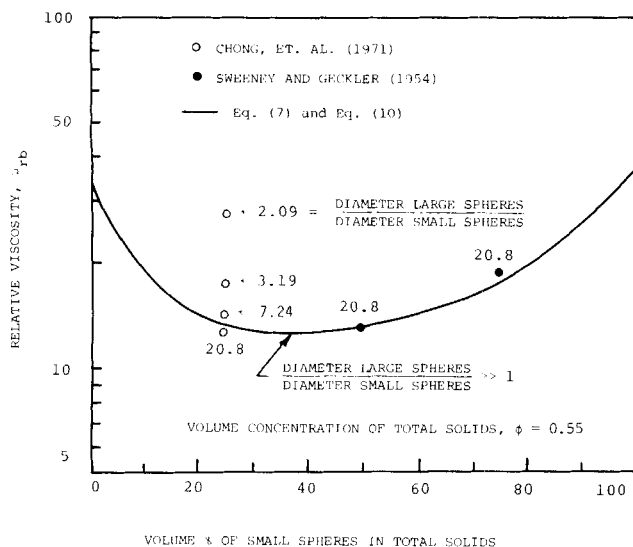


Fig. 3. Relative viscosity in bidispersed system for mixtures with volume concentration of total solids, $\phi = 0.55$.

would be some value of ϕ between the two extremes obtained from the cubic and rhombohedral particle packings. Bagnold (1954, 1966) also found experimentally that $\phi = 0.625$ represented the upper limit of the solids concentration when general shearing first becomes possible in a mixture formed of granular solids and a surrounding fluid. Figure 2 shows that Equation (7) provides an excellent approximation to the experimental data at virtually all concentrations. The asymptotic formula obtained by Frankel and Acrivos (1967) and the formulas of Einstein (1956) are also presented. For monodispersed systems, Thomas reported that the relative viscosity is independent of particle size and is a function of only particle concentration. At the concentration of 62.5% by volume of solids, Thomas reported that the relative viscosity approached infinity asymptotically.

POLYDISPERSED SYSTEMS

Consider a mixture of suspended solids in which the particles consist of spheres having different diameters. For suspensions containing particles of differing diameters, the theoretical description of the local velocity gradients would then be more complex than those shown in Equation (3), and the resulting equations for effective viscosity would correspondingly be more involved than that given by Equation (7). The term μ_r would be a function of particle size distribution within the mixture as well as total concentration ϕ of solids. If a bidispersed system is considered, however, where, in a relative sense, only very large and very small particles form the solid portion of the mixture, the analysis for the effective viscosity is reduced again to one of relative simplicity. Consider a mix-

ture having a total solids concentration ϕ , of which ϕ_s is the concentration of the very small particles and ϕ_b is the concentration of the very large particles. The small particles and the fluid occupy a percentage of the total volume equal to $1 - (\phi - \phi_s)$. In the local environment of the fluid and small particles, the small particles have a concentration

$$\phi_{rs} = \frac{\phi_s}{1 + \phi_s - \phi}$$

If the shape of large and small particles are identical, then the maximum attainable concentration ϕ_m can be assumed to be the same for both large and small particles.

Using an equation similar to Equation (6) to describe the shear stress in a bidispersed system, we get

$$\tau_{\mu} = \mu_0 \mu_r(\phi_{rs}, \phi_m) \mu_r(\phi - \phi_s, \phi_m) \frac{du}{dy} \quad (9)$$

The effective viscosity μ_{rb} of a bidispersed system can therefore be described as

$$\mu_{rb} = \mu_r(\phi_{rs}, \phi_m) \mu_r(\phi - \phi_s, \phi_m) \quad (10)$$

where μ_r is the effective viscosity of a monodispersed system. The effective viscosity of the bidispersed system described by Equation (10) is compared in Figure 3 to experimentally determined values obtained from results reported by Chong, Christiansen, and Baer (1971) and Sweeney and Geckler (1954) for tests where the total solids concentration was $\phi = 0.55$. In those tests, the ratio between large and small particle diameters varied between 2.09 and 20.8. The solid curve in Figure 3 is obtained using Equations (10) and (7) to describe the value of μ_{rb} and provides an excellent comparison with all of the experimental data found to be available when the ratio of large and small particle diameters becomes much larger than unity, a condition which satisfies the basis for the analysis leading to the development of Equation (10).

INERTIA DOMINATED REGION

The cubic packing shown in Figure 1a was used to describe the time averaged particle orientation representative of the geometric conditions that were assumed to exist when viscous effects predominated. As strain rates increase, collisions between adjacent spherical particles become more common. At sufficiently high strain rates, the effects of mechanical interaction between particles can become a significant factor in determining the rheological properties of a solid-liquid mixture (Bagnold, 1954). The mechanism by which particle collisions are produced can be described by considering the motion of the solid particles having a cubic packing oriented with respect to the direction of the flow field as shown in Figure 4a. The geometry is considered to be representative of particle orientation when interparticle collisions play a significant role in determining the mixture properties. As shown in Figure 4b, the relative velocity of particle C with respect to B is $(\alpha d/\sqrt{2}) du/dy$. On the average, particles make $(\alpha d/\sqrt{2}) du/dy / (2\alpha d/\sqrt{2})$ collisions per second with particles at a lower level. Each collision of a particle of mass m results in a reduction of the x component of its momentum by the amount $m(1 - \cos\beta) \alpha d/\sqrt{2} du/dy$. Within the volume $(\alpha d)^3$ there are $\phi(\alpha d)^2/\pi d^3/6$ particles of density ρ_s . The force F_i acting over the area $2(\alpha d)^2$ which is necessary to sustain the particle motion is, therefore

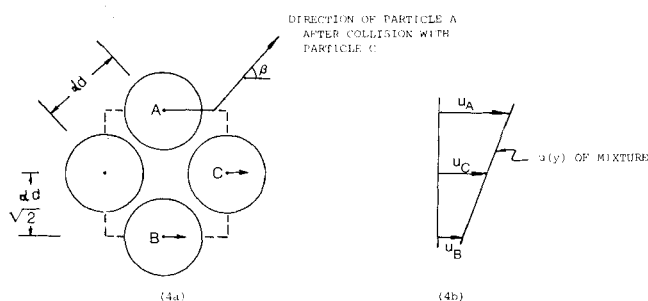


Fig. 4. Orientation of particles in inertia dominated region.

$$F_i = \left[m(1 - \cos\beta) \frac{\alpha d}{\sqrt{2}} \frac{du}{dy} \right] \left[\frac{\alpha d}{\sqrt{2}} \frac{du}{dy} \right] \left[\frac{2\alpha d}{\sqrt{2}} \right] \left[(\alpha d)^3 \phi \left/ \frac{\pi d^3}{6} \right. \right] \quad (11)$$

Since the mass of a single spherical element is $m = \rho_s \pi d^3/6$, Equation (11) becomes

$$F_i = \rho_s \left(\frac{1 - \cos\beta}{2\sqrt{2}} \right) (\alpha d)^4 \phi \left(\frac{du}{dy} \right)^2 \quad (12)$$

The inertial contribution to the shear stress τ_i necessary to sustain a movement of a mixture having a velocity gradient du/dy therefore becomes

$$\tau_i = \rho_s \left(\frac{1 - \cos\beta}{4} \right) \phi (\alpha d)^2 \left(\frac{du}{dy} \right)^2 \quad (13)$$

If the added mass of the fluid associated with each sphere is included when determining the stresses produced by particle collisions, we get

$$\tau_i = (\rho_s + k_1 \rho_f) \left(\frac{1 - \cos\beta}{4} \right) \phi (\alpha d)^2 \left(\frac{du}{dy} \right)^2 \quad (14)$$

In Equation (14), k_1 is the added mass coefficient associated with spheres within the solid-liquid mixture. A value for which k_1 which is considered appropriate for the added mass factor is that used for a sphere of diameter d having concentric centers with a larger bounding sphere of diameter D (Lamb, 1932). In the present context, the larger sphere can be considered to consist of the combination of surfaces formed by those grains which surround any other suspended particle within the solid-liquid mixture. Letting $D = \alpha d$, we get

$$k_1 = \frac{1}{2} \left[\frac{\alpha^3 + 2}{\alpha^3 - 1} \right] \quad (15)$$

Substituting Equations (15) and (8) into Equation (14), we get

$$\tau_i = \left[\rho_s + \frac{1}{2} \left(\frac{\phi_s + 2\phi}{\phi_s - \phi} \right) \rho_f \right] \left(\frac{1 - \cos\beta}{4} \right) \phi_s^{2/3} \phi^{1/3} d^2 \left(\frac{du}{dy} \right)^2 \quad (16)$$

The representative value of $\cos\beta$ is expected to be dependent upon the solid concentration within the mixture. Experimental evidence is necessary in order to confirm the validity of the relationship described by Equation (16). This equation indicates that inertial effects influencing the constitutive relationship of a solid-liquid mixture produce non-Newtonian characteristics. Such phenomena have been observed by previous experimentors, as reported by Jeffrey and Acrivos (1976). The shear thickening behavior of solid-liquid mixtures as well as the rapid increase in shear stress with high values of solid concentration, as reported by Metzner and Whitlock (1958), are phenomena which are consistent with results indicated by Equation (16).

FLOW REGIME INDICATOR

The value of the parameter $R = \tau_i/\tau_\mu$ should provide a guide for determining whether or not the resistance to the flow of the mixture is dominated by viscous or inertia effects. Solving for R , we get

$$R = \left[\frac{\rho_s}{\rho_f} + \frac{1}{2} \left(\frac{\phi_s + 2\phi}{\phi_s - \phi} \right) \right] \left[\frac{(1 - \cos\beta) \phi_s^{2/3} \phi^{1/3}}{4\mu_r(\phi, \phi_s)} \right] \left[\frac{d^2}{\nu_o} \frac{du}{dy} \right] \quad (17)$$

If we combine the concentration and density dependent terms into a single variable f , Equation (17) reduces to

$$R = f \left(\phi, \phi_s, \frac{\rho_s}{\rho_f} \right) \frac{d^2}{\nu_o} \frac{du}{dy} \quad (18)$$

The role of R in differentiating the regions where viscous and inertia dominated effects prevail will require considerable experimental study. The utility of quantitatively identifying such a parameter would be that flow regimes could be identified for which either Equation (6) or Equation (16) can be used to determine the relationship between shear stress and strain rate.

NOTATION

d	= particle diameter
F	= shearing force on an element of the mixture
G	= local velocity gradient
K_1	= added mass coefficient
R	= τ_i/τ_μ = dimensionless parameter
u	= velocity of the mixture
x, y, z	= Cartesian coordinates

Greek Letters

α	= $(\phi_s/\phi)^{1/3}$
μ^*	= effective viscosity of the mixture
μ_o	= viscosity of the suspending fluid
μ_r	= μ^*/μ_o
τ	= shear stress
τ_i	= shear stress due to inertia effects
τ_μ	= shear stress due to viscous effects
ϕ	= volume concentration of solids
ϕ_s	= maximum attainable concentration
ϕ_{rs}	= relative concentration of small particles in bidispersive mixtures

Symbols

— = average

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Effective Interfacial Area Determination by Gas Absorption Accompanied by Second-Order Irreversible Chemical Reaction

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Oxygen and carbon dioxide were absorbed by aqueous sodium hydroxide solutions in an agitated vessel, and the experimental results were interpreted in terms of the surface renewal theory in order to deduce effective interfacial areas. The simultaneous physical and chemical absorption experiments permitted a determination of the enhancement factor under identical physicochemical and hydrodynamic conditions. It was found that for the unbroken interface case, the effective areas for physical and chemical absorption are equal when the Danckwerts parameter γ is approximately unity. γ is defined as the ratio of the increase in absorption capacity of the liquid to the enhancement factor. For the case where the gas is sparged through the liquid, it was found that the effective interfacial area is a strong function of agitator speed (above a critical speed) and gas flow rate, whereas the mass transfer coefficient was found to be nearly independent of agitator speed and gas sparge rate.

SCOPE

$$a = k_c^\circ a / k_c^\circ$$

The interfacial area effective for mass transfer was measured for gas absorption in an agitated vessel. Experimental enhancement factors were determined for the irreversible second-order reaction between carbon dioxide and sodium hydroxide. Physical and chemical absorption rates were measured under identical physicochemical and hydrodynamic conditions by the simultaneous chemical absorption of carbon dioxide and the physical absorption or desorption of oxygen in aqueous solutions. The experimental enhancement factors together with theoretical solutions of the partial differential equations describing absorption accompanied by an irreversible second-order reaction according to the Higbie penetration or Danckwerts surface renewal theories allows an evaluation of the penetration time or surface renewal rate. The physical absorption mass transfer coefficient k_c° may then be predicted from a knowledge of the rate of surface renewal. Thus the effective interfacial areas may be determined from the measured values of the mass transfer coefficient times the effective interfacial area $k_c^\circ a$ and the predicted values of the mass transfer coefficient:

Danckwerts and Joosten (1973) hypothesize that the effective area for chemical reaction depends on the type of reaction through the parameter γ , where γ is defined as the ratio of the factor by which the reaction increases the capacity of the liquid to absorb to the factor by which the reaction increases the rate of absorption:

$$\gamma = C/E$$

Experiments by Danckwerts and Joosten in a packed column show that when $\gamma \approx 1$, the effective area for chemical absorption is equal to that for physical absorption and that when $\gamma \gg 1$, the effective area is significantly greater for chemical absorption than for physical absorption. The reaction studied in this work, $\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$, was chosen because it gives values of γ near unity. Previously used chemical absorption methods for determining effective interfacial areas have employed absorption accompanied by a rapid first-order chemical reaction with $\gamma \gg 1$.

Experiments were carried out in an agitated vessel for the case of absorption across an unbroken interface and for the case where the gas is sparged through the liquid.