θ = angular direction
ϕ = axial direction
$'$ = dimensional quantity

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Manuscript received June 9, 1978; revision received December 7, and accepted January 11, 1979.

A Study of Disaggregation Effects in Sedimentation

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Aggregates are considered as a porous medium. Stresses within the porous solid matrix are calculated when the particle deformation is ignored. The maximum size of the aggregates is derived from a yield condition, and the settling velocity is deduced. The influence of the mechanical properties and concentration of the aggregates are detailed and discussed.

SCOPE

Sedimentation plays an important role in many chemical engineering processes and is also important in medicine (where erythrocyte sedimentation has become a standard clinical test) and in meteorology. The aggregation of particles or formation of clusters has long been recognized as an important factor when dealing with particles suspended in liquids.

Hence, the main objectives of this work are to gain insight into the mechanisms involved and to predict the maximum size of an aggregate when it settles. The aggregate is broken by forces generated by the motion; the larger the aggregate, the larger its settling velocity and thus the larger are these rupture forces. Consequently, we need a model to describe the flow within the aggregate and a model to relate the breakup of the aggregate to the flow field.

More precisely, the flow inside the aggregate, considered as a porous medium, is described by a Brinkman equation. The free cell model is then used to predict the velocity and pressure fields inside and outside the porous medium. Stresses within the porous solid matrix are gen-

erated by the fluid motion through the aggregate; they are calculated when the particle deformation is neglected.

The aggregate is supposed to break up when the distortion energy has reached a certain value characteristic of the material. The maximum size of the aggregates and the settling velocity can thus be derived.

CONCLUSIONS AND SIGNIFICANCE

The maximum size of the aggregates is shown to be a function of two dimensionless parameters, the volume concentration of the aggregates and the ratio of hydrodynamic forces to cohesive forces. The dependence of size and maximum settling velocity on these parameters are given.

If the mechanical properties of the aggregate, such as its porosity, are assumed to be constant, it is shown that the dimensionless radius of the aggregate varies directly with concentration. Thus, the settling rate decreases more slowly than in permanent aggregates since the apparent weight increases with concentration. However, the variations in the settling rate are still much greater than the variations in the viscosity of an aggregable suspension with concentration. Hence, the settling rate magnifies the variations in mechanical properties or concentration. This magnification is probably related to the poor reproducibility of settling experiments.

The size of the aggregate is shown to be always finite, whatever the value of the dimensionless parameters, which is an important difference with sheared suspensions.

The main limitations of the present calculations are pointed out.

Because of their practical applications, suspensions have received much attention in recent years (see review articles Batchelor, 1976, and Jeffrey and Acrivos, 1976). Many of them are aggregable suspensions, and this property plays a key role in the mechanical properties at low shear rates; an illustrative example is blood (Goldsmith and Skalak, 1973), but simpler ones can be cited (Kao et al., Gillespie, 1963; Lewis and Nielsen, 1968).

The sedimentation, or settling, of a suspension plays an important role in many chemical engineering processes. The aggregation of particles has long been recognized as an important factor when dealing with particles suspended in liquids, and the settling velocity can be drastically modified.

The purpose of this paper is to take into account the influence of the disaggregation on the settling rate of aggregable suspensions; the aggregates are supposed to be broken by the hydrodynamic forces which are generated by the fluid motion. We shall thus calculate the maximum size and the maximum settling rate of such suspensions as a function of the mechanical properties of the aggregate. This paper can also be considered as an extension of the results obtained for the viscosity of aggregable suspensions (Adler, 1978; Adler and Mills, 1979).

The model includes some important steps.

In order to account for the presence of fluid within the aggregate, it will be viewed as a porous medium. The free cell model of Happel (1958) is used to calculate the hydrodynamic properties of the suspension; the results of Neale et al. (1973) are then applied. This model assumes that the disturbance due to the presence of each particle is confined to a cell of fluid bounded by a frictionless envelope on whose surface the normal disturbance velocity vanishes. The outer fluid shell is assumed to enclose an amount of fluid such that the fluid-solid volume ratio in the cell is identical to that in suspension.

This kind of model suffers some drawbacks, since the results strongly depend on the choice for the shape of the cell and the boundary conditions; moreover, derived results disagree with Einstein's at low concentrations and with experimental results at high concentrations. However, it should be stressed that the order of magnitude of the settling velocity is correct for intermediate concentrations and that such a model provides the flow field within the aggregate, an essential feature in order to calculate the forces exerted by the fluid upon the aggregate.

The porous solid matrix of the aggregate is considered as an elastic solid characterized by its Lamé moduli. Moreover, the cohesive forces which prevent disaggregation will be introduced as a yield condition on the stresses existing in the solid porous matrix. The maximum size of the aggregate is derived from this yield condition.

In this paper, basic equations for the flow fields inside and outside a porous sphere are reviewed; the stresses within the porous matrix are determined from the displacement field equation. The solution to the hydrodynamic problem is noted, and stresses in the porous matrix are derived, assuming that the sphere is only slightly deformed; the yield stress condition is then calculated. Numerical results for the dimensionless radius and settling rates of the aggregates are presented and discussed.

BASIC EQUATIONS AND HYPOTHESES

The spherical aggregate is considered as a porous medium. The equation of motion most widely adopted to describe creeping Newtonian flow through an isotropic porous medium is the empirical Darcy law. However, this law is generally considered to be somewhat uncertain near the surface of bounded porous media, since it is not of a sufficiently high order to entertain boundary conditions on the shear stress. In our case, according to Neale et al. (1973), Brinkman's extension of the Darcy law is preferable; this was recently experimentally confirmed for a single isolated permeable sphere (Matsumoto and Suganuma, 1977). Moreover, the Brinkman equation has recently received theoretical justification (see, for instance, Saffman, 1971).

Some cell models can be used for calculating the settling rate of an aggregable suspension. The free cell model of Happel (1958) was used for aggregates by Neale et al. (1973); the self-consistent model of Neale and Nader (1974) was applied to the same physical situation by Adler et al. (1978). The two models were compared in this last paper; it was concluded that since in the case of gravitational settling c is very rarely greater than 0.4, the results of the two models are, practically

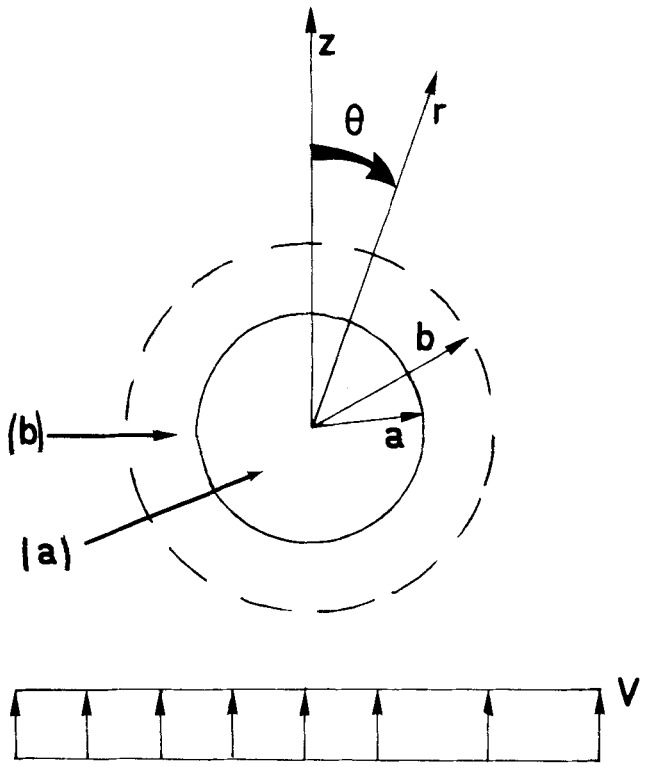

Fig. 1. Description of the modeled system; $a = b.c^{1/3}$. *(a)* reference sphere of permeability k; *(b)* fluid region.

speaking, virtually indistinguishable. The free cell model is thus used here, since the numerical calculations are simpler.

Hence, let us consider a porous sphere of radius a and permeability k, which is immersed in an incompressible Newtonian fluid of viscosity μ. When the free cell model is used, the porous sphere is surrounded by a frictionless envelope of radius b (Figure 1).

The only external force which acts on the sphere is gravity, but no external couple acts on it. The Reynolds number of the fluid motion is supposed to be small, and thus inertia forces can be ignored.

Let us recall the following set of familiar equations for the two zones of the model which are sketched in Figure 1 (Neale et al., 1973):

$$a \leq r \leq b: \quad \nabla \bar{p} = \mu \nabla^2 \bar{\mathbf{u}}; \quad \nabla \cdot \bar{\mathbf{u}} = 0 \tag{1a}$$

$$r \leq a: \quad \nabla \tilde{p} = \mu \nabla^2 \tilde{\mathbf{u}} - \frac{\mu}{k} \cdot \tilde{\mathbf{u}}; \quad \nabla \cdot \tilde{\mathbf{u}} = 0 \tag{1b}$$

Boundary conditions for the flow fields in the free cell model are the following:

$$r = a: \quad \tilde{\mathbf{u}}(\mathbf{x}) = \bar{\mathbf{u}}(\mathbf{x}); \quad \overline{\boldsymbol{\Pi}} \cdot \mathbf{x} = \tilde{\boldsymbol{\Pi}} \cdot \mathbf{x} \tag{2a}$$

$$r = b: \quad \bar{u}_r = V \cos\theta; \quad \overline{\Pi}_{r\theta} = 0 \tag{2b}$$

The solution to the hydrodynamic problem defined by Equations (1) and (2) will be briefly recalled in the next paragraph.

The mechanical problem consists of calculating the stresses σ inside the porous solid matrix. It is equivalent to consider each phase as a continuum or only the fluid-particle system as a continuum, as shown by Atkin and Craine (1976). From the former standpoint, it can be said that the stresses σ are generated by the fluid motion; the hydrodynamic force exerted by the fluid upon the solid per unit volume is equal to $\mu\tilde{\mathbf{u}}/k$. To this resistance should be added the apparent weight per unit volume of the porous medium $(\rho_S - \rho_L)(1 - \epsilon)\mathbf{g}$. The stress tensor σ is assumed to be a linear and isotropic function of the strain $\boldsymbol{\varepsilon}$ (Biot, 1955):

$$\sigma = 2m\boldsymbol{\varepsilon} + \rho \cdot t_r(\boldsymbol{\varepsilon}) \cdot 1 \tag{3a}$$

If N is defined by

$$N = \frac{l}{2(p+m)} \tag{3b}$$

and if the elastic field is assumed to be positive definite, then N ranges from -1 to $\frac{1}{2}$ (Gurtin, 1972). N can be approximately considered as a measure of the compressibility of the elastic material.

The equilibrium equation for the stresses is derived from (3) and expressed in terms of the displacement field $\mathbf{d}$ as (Gurtin, 1972)

$$\nabla^2 \mathbf{d} + \frac{1}{1-2N} \cdot \nabla(\nabla \cdot \mathbf{d}) + \frac{\mu}{m} \cdot \frac{\tilde{\mathbf{u}}}{k} + \frac{(\rho_S - \rho_L)(1-\epsilon)}{m} \cdot \mathbf{g} = 0 \tag{4}$$

The boundary condition when $r = a$ for the stress must still be expressed. The only forcing for the stress in the solid derives from the effective body force; the external fluid stress traction is balanced by the internal stress traction in (2a). Thus, $\sigma \cdot \mathbf{x}$ should be equated to 0; that is

$$\underline{\sigma} \cdot \mathbf{x} = 0 \quad \text{at} \quad r = a \tag{5}$$

The yield condition characterizing the cohesive forces which prevent disaggregation is taken to be the Mises yield condition:

$$t_r(\sigma_D^2) \leq 2T^2 \tag{6}$$

where T is the yield value characteristic of the porous solid matrix. This condition states that the yield limit is reached when the distortion energy has reached a certain value characteristic to the material.

The deformation of the particle is henceforth neglected. The porous particle is assumed to remain approximately spherical until it breaks. This condition will be clarified later.

SOLUTIONS OF THE HYDRODYNAMIC AND MECHANICAL PROBLEMS

For the sake of brevity, these solutions are expressed in terms of spherical harmonics.

The velocity and the pressure field inside the porous sphere were derived by Neale et al. (1973); they can be expressed as

$$\tilde{\mathbf{u}} = -\frac{k}{\mu} \cdot \nabla \tilde{p}_1 + 2\psi_0(\xi) \cdot \nabla\tilde{\phi}_1 + \psi_2(\xi) \cdot \frac{r^5}{k} \cdot \nabla\left(\frac{\tilde{\phi}_1}{r^3}\right) \tag{7a}$$

$$\tilde{p} = \tilde{p}_1 \tag{7b}$$

All the relevant quantities such as the functions ψ_i and the spherical harmonics $\tilde{\phi}_1$, $\tilde{p}_1$ are detailed in Appendix A. ψ_i are only functions of the radial dimensionless coordinate ξ, while $\tilde{\phi}_1$ and $\tilde{p}_1$ depend on the dimensionless radius of the aggregate ξ_1 and on the concentration.

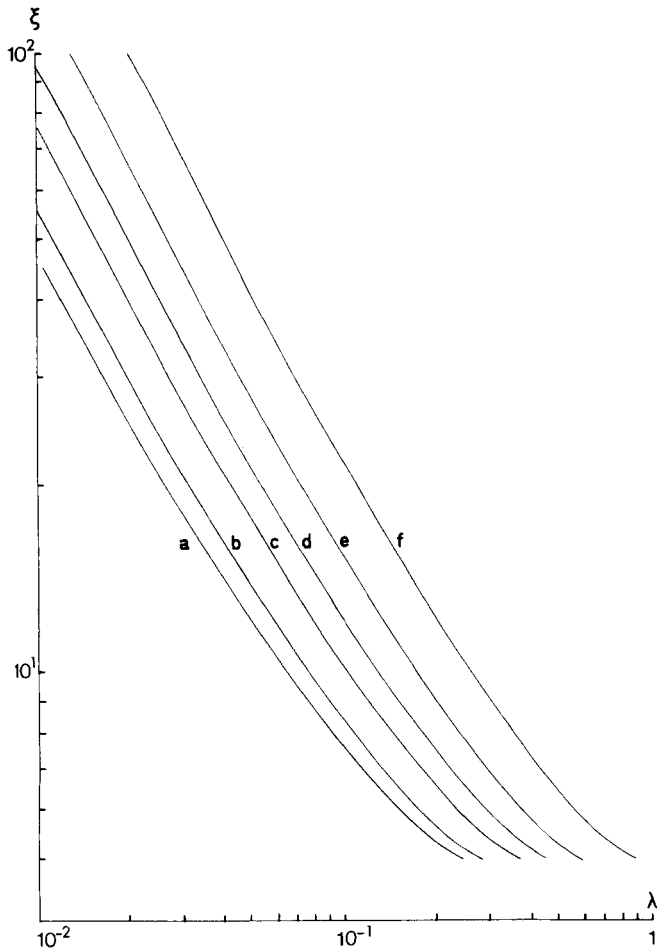

Fig. 2. Dimensionless radius ξ of the aggregate as a function of λ and of the concentration c. Values of c are 0.1 (a), 0.3 (b), 0.5 (c), 0.6 (d), 0.7 (e), 0.8 (f).

The sedimentation rate is given by the familiar equation

$$V = \frac{\xi_1^2}{\Omega} \cdot V_0 \qquad (8a)$$

where Ω is a dimensionless function of ξ_1 and c which is given in Appendix A. V_0 is a reference velocity expressed as

$$V_0 = \frac{2}{9} \cdot \frac{(\rho_S - \rho_L) g (1-\epsilon) k}{\mu} \qquad (8b)$$

which can be viewed as the settling velocity of a sphere of radius $\sqrt{k}$ when the density difference is $(\rho_S - \rho_L)(1-\epsilon)$.

When the velocity field is known, the stress tensor in the porous solid matrix can be derived as it is outlined in Appendix B. Then the deviatoric part σ_D of this stress tensor can be expressed as

$$\sigma_D = -\mu[\nabla \tilde{u} + (\nabla \tilde{u})^t] + T\left[\mathbf{x}\nabla \tilde{p}_1 + (\mathbf{x}\nabla \tilde{p}_1)^t - \frac{2}{3}\tilde{p}_1 \cdot 1\right] \qquad (9)$$

As an application of these results, let us consider a suspension of porous spheres which are settling in a fluid.

Lengthy but straightforward calculations lead to an explicit expression for the yield condition (6). Velocity is obtained from Equation (7a); the rate of strain tensor in the fluid is then calculated. From expression (7b) for the pressure field, we can obtain the deviatoric part of the

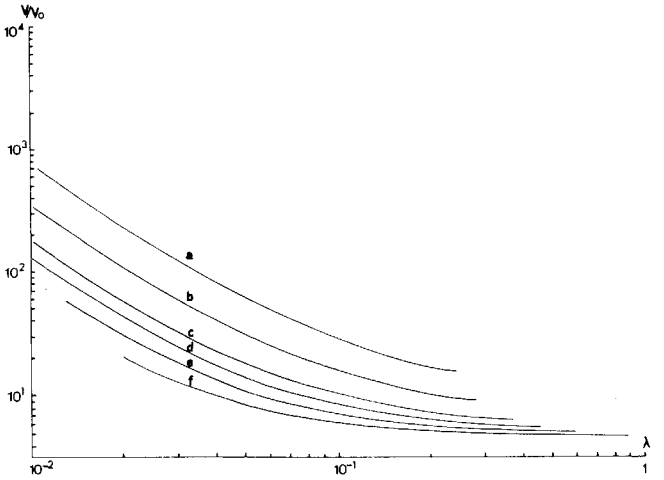

Fig. 3. Dimensionless settling velocity V/V_0 of the aggregates as a function of λ and of the concentration c. Values of c are given in Figure 2.

stress tensor in the porous solid matrix through (9). Finally, $t_r(\sigma_D^2)$ is calculated, and the yield condition is deduced as

$$\mathcal{L} + \xi^2 \cdot \cos^2\theta \cdot \mathcal{M} \leq 2 \cdot \left(\frac{T\sqrt{k}}{\mu H V}\right)^2 \qquad (10)$$

$\mathcal{L}$ and $\mathcal{M}$ are defined in Appendix B; they are only functions of ξ, ξ_1, and c.

The maximum size of the aggregate is determined from (8) and (10). More precisely, one must first determine the maximum value of the left-hand side of (10) when ξ ranges from 0 to ξ_1. Thus, the maximum radius of the aggregate is the solution of the implicit equation

$$\frac{V_0 \mu}{\sqrt{2}\sqrt{k} T} = \frac{\Omega}{\xi_1^2 |H| \sqrt{f}} \qquad (11)$$

When ξ_1 is known, the settling rate is derived from (8).

Dimensionless parameters of the problem can now be listed. It should first be emphasized that the material constant N, which is characteristic of the mechanical properties of the porous matrix, does not appear in the final result (11), but the complete stress tensor σ does depend on N. It was assumed that the deformation could be ignored. This is equivalent to assuming that the parameter T/m is very small; the problem was solved at the first order in terms of this parameter.

The left-hand side of (11) is a dimensionless quantity λ which can be considered as the ratio of hydrodynamic forces to cohesive forces in the aggregate. As is clear from (11), the solution ξ_1 of the problem only depends on the concentration c and on λ.

It should be noticed that λ is representative of the mechanical properties of the aggregate. The value of T could be determined theoretically from the knowledge of the forces exerted between two elements of the aggregate; an example of such a calculation is given by Firth and Hunter (1976) but under rather different hypotheses.

Numerical results for the dimensionless radius and the settling velocities will be presented in the next paragraph.

RESULTS AND DISCUSSION

With respect to the complexity of Equations (11) and (8), the consequences of the previous analysis are mainly numerically explored. Moreover, results are limited to ξ_1 ranging from 5 to 100.

The dimensionless radius of the aggregate is plotted in Figure 2 as a function of c and λ. It is seen that ξ_1 varies

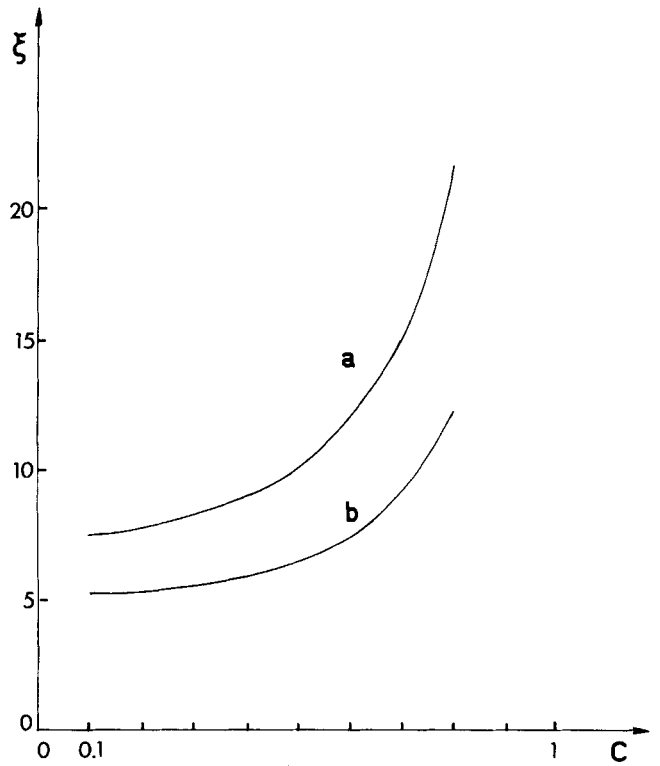

Fig. 4. Dimensionless radius of the aggregate as a function of the concentration. Values of λ are 0.1 *(a)*, 0.2 *(b)*.

directly with concentration, a point which will be resumed below; ξ_1 varies inversely with λ. This was physically expected, since the larger are the aggregation forces, the lower is λ. It should be noted that ξ_1 is a very steep function of c and λ when λ is small.

The dimensionless settling rate is represented in Figure 3 as a function of the same parameters; V/V_0 varies inversely with c and λ.

Let us now assume that the mechanical properties of the aggregate do not depend on the concentration; that is, for a given suspension, λ is a constant. An illustrative example of the influence of the concentration on the dimensionless radius and the settling velocity is given in Figures 4 and 5.

Finally, analytical formulas were derived for large aggregates in order to check our calculations and to obtain information about limiting cases. It was numerically shown that the yield condition was fulnlled for $\xi = \xi_1$ and in the equatorial plane when ξ_1 is large. Their derivation from (8) and (10) is then straightforward; they can be expressed as

$$\xi_1 = \frac{1}{6} \cdot \sqrt{\frac{2}{3}} \cdot \frac{3 + 2\eta^5}{1 - \eta^5} \cdot \frac{\sqrt{2k}\ T}{V_{0\mu}} \qquad (12)$$

$$\frac{V}{V_0} = \frac{3}{2} \cdot \frac{2 - 3\eta + 3\eta^5 - 2\eta^6}{3 + 2\eta^5} \cdot \xi_1^2 \qquad (13)$$

However, care should be observed in the practical use of the above formulas; η should not approach 1.

It is interesting to compare these results with those obtained for the viscosity of concentrated suspensions of aggregable particles (Adler, 1978).

Firstly, it has been shown that the radius of an aggregate in a shear flow can theoretically be infinite if the shear is small enough. For a settling suspension, Equation (12) shows that there is no lower bound for λ, below which the aggregate grows indefinitely. In this case, the hydrodynamic forces always play an important role in limiting the size of the aggregates.

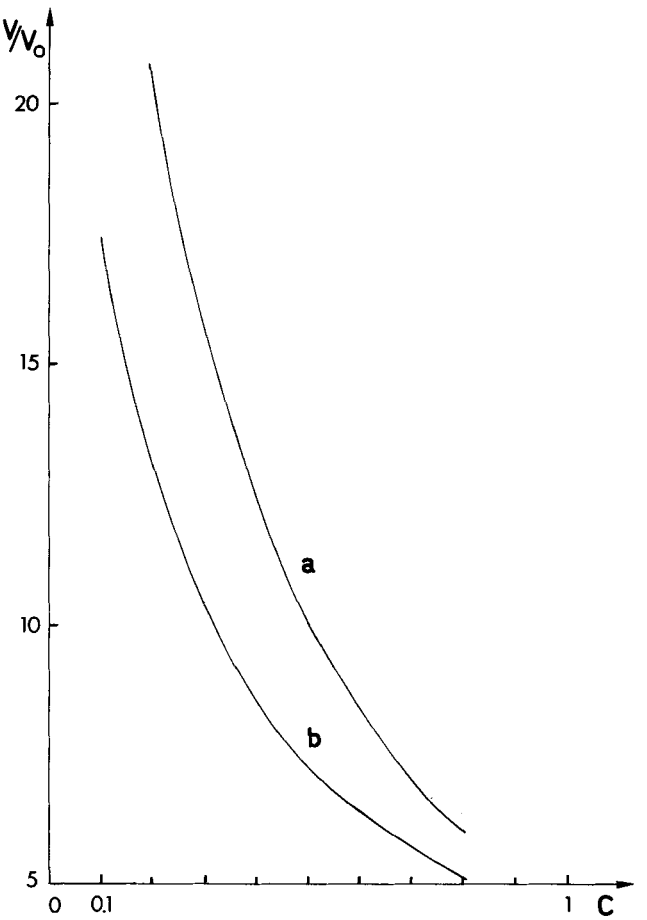

Fig. 5. Dimensionless settling velocity as a function of the concentration. Values of λ are given in Figure 4.

The second important difference with a shear flow is that the aggregate grows when concentration increases, while in a shear the aggregate becomes progressively thinner. In the present case, the size of the aggregate is determined by two opposite effects; when the concentration increases, the aggregate falls slower and hence the hydrodynamic forces are reduced. But with respect to the increase in concentration, these forces are magnified. Hence, the present calculations show that the first effect is predominant when it is assumed that the mechanical properties of the aggregates do not depend on the concentration variation.

This implies that the relative variations in the settling rate are narrower than for permanent aggregates. However, it should be emphasized that the variations in the settling rate are much wider than the corresponding variations in viscosity. The settling rate magnifies the variations in concentration and mechanical properties. Moreover, results for the settling rate are simpler since they do not depend on the material constant N.

This magnification by the settling velocity surely plays an important role in its well-known poor reproducibility. It is clear from Figures 2 and 3 that for small values of λ, a small variation in concentration or mechanical properties causes a large variation in size and settling rate. Moreover, in any real system, the suspension cannot be perfectly homogeneous.

However, the previous results must be somewhat limited.

From a mechanical standpoint, it should be recalled that the deformation of the porous matrix was assumed to be negligible. Hence, these results cannot be applied to cases where deformation is expected to be large, such as polymer coils. However, they surely provide a good first

approximation for other physical situations, for example, porous spheres made of small impermeable spheres.

The results and conclusions were only derived for the maximum admissible size of the aggregate. The phenomenon of collision is not taken into account in the present calculations.

Finally, the electrokinetic phenomena liable to be present in the aggregation are not taken into account here, though their influence on the settling velocity can be significant. The reader is referred to the work of Levine et al. (1976).

NOTATION

a = radius of the aggregate
b = $a/c^{1/3}$ = radius of the cell
c = volume concentration of aggregates
$\mathbf{d}$ = displacement field
f = maximum value of left-hand side of formula (10) when ξ ranges from 0 to ξ_1
F, H = functions of ξ_1 and c defined in Appendix A
$\mathbf{g}$ = acceleration of gravity
k = permeability of the aggregates
l, m = Lamé moduli
$\mathcal{L}, \mathcal{M}$ = functions of ξ, ξ_1 and c defined by (B5)
N = material constant defined by $(3b)$
p = pressure
$\tilde{p}_1$ = solid spherical harmonic of order 1 (see Appendix A)
r = radial coordinate (Figure 1)
T = yield value
T = function of ξ_1 and c defined by (B4)
$\mathbf{u}$ = velocity
V = settling velocity
V_0 = reference velocity defined by $(8b)$
$\mathbf{x}$ = Cartesian coordinate system (Figure 1)

Greek Letters

ϵ = porosity of the aggregate
$\boldsymbol{\varepsilon}$ = strain tensor in the solid porous matrix
η = $c^{1/3}$
θ = polar direction
λ = $V_0\,\mu/\sqrt{2k}\;T$
μ = dynamic viscosity of the liquid
ξ = $r/\sqrt{k}$
ξ_1 = $a/\sqrt{k}$
$\mathbf{II}$ = stress tensor in the fluid
ρ_S, ρ_L = density of the solid and liquid phase, respectively
$\boldsymbol{\sigma}$ = stress tensor in the porous solid matrix
$\boldsymbol{\sigma}_D$ = deviatoric part of $\boldsymbol{\sigma}$
$\tilde{\phi}_1$ = solid spherical harmonic of order 1 defined in Appendix A
ψ_i = function of ξ defined in Appendix A
$\hat{\psi}_i$ = $\psi_i(\xi_1)$
Ω = defined in Appendix A

Superscripts

$\sim$, $\wedge$ = inner permeable sphere, the fluid region in the cell

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APPENDIX A

The solid spherical harmonics of order I can be expressed as

$$\tilde{p}_1 = \frac{\mu}{k} \cdot F.V.z$$

$$\tilde{\phi}_1 = \frac{1}{6} \cdot H.V.z$$

F and H are deduced from

$$J = 2\xi_1{}^2 - 3\xi_1{}^2\eta + 3\xi_1{}^2\eta^5 - 2\xi_1{}^2\eta^6 + 90\xi_1{}^{-2}\eta^5 + 42\eta^5 - 30\eta^6 + 3 - \frac{th\xi_1}{\xi_1} \cdot (-3\xi_1{}^2\eta + 15\xi_1{}^2\eta^5 - 12\xi_1{}^2\eta^6 + 90\xi_1{}^{-2}\eta^5 + 72\eta^5 - 30\eta^6 + 3)$$

$$A = -\frac{1}{J}\left[\xi_1{}^5 + 6\xi_1{}^3 - \frac{th\xi_1}{\xi_1} \cdot (3\xi_1{}^5 + 6\xi_1{}^3)\right]$$

$$B = \frac{1}{J} \cdot \left[3\xi_1{}^3 + 2\xi_1{}^3\eta^5 + 30\xi_1\eta^5 - \frac{th\xi_1}{\xi_1} \cdot (3\xi_1{}^3 + 12\xi_1{}^3\eta^5 + 30\xi_1\eta^5)\right]$$

$$F = -\frac{B}{\xi_1{}^3} + \frac{10\eta^5 A}{\xi^5}; \quad H = \frac{6\xi_1{}^2}{Jch\xi_1} \cdot (1 - \eta^5)$$

The function $\psi_n(\xi)$ is given by

$$\psi_n(\xi) = \left(\frac{1}{\xi}\cdot\frac{d}{d\xi}\right)^n \frac{sh\xi}{\xi}$$

Finally, Ω is expressed as

$$\Omega = \frac{2B}{3\xi_1}$$

APPENDIX B. DERIVATION OF THE STRESS TENSOR AND OF THE YIELD CONDITION

Equation (4) together with boundary conditions (5) should be solved in order to obtain the stresses in the solid matrix, when deformation of the particle is neglected.

A mathematically complete solution of Equation (4) is the Boussinesq-Papkovitch-Neuber solution (Gurtin, 1972); the displacement field d is expressed as

$$\mathbf{d} = \Psi^\circ - \frac{1}{4(1-N)}\cdot\nabla(\mathbf{x}\cdot\Psi^\circ + \varphi) \qquad (B1)$$

where φ and Ψ° are scalar and vector fields that satisfy

$$\nabla^2\varphi = \frac{\mu}{mk}\cdot\mathbf{x}\cdot\tilde{\mathbf{u}} + \frac{(\rho_S-\rho_L)(1-\epsilon)gz}{m} \qquad (B2a)$$

$$\nabla^2\Psi^\circ = -\frac{\mu}{mk}\tilde{\mathbf{u}} - \frac{(\rho_S-\rho_L)(1-\epsilon)}{m}\cdot\mathbf{g} \qquad (B2b)$$

Particular solutions of these equations with second member can be easily found, since $\tilde{\mathbf{u}}$ satisfies Brinkman equation (1b) and $\tilde{p}$ is a harmonic field which can be expanded as a sum of solid spherical harmonics $\tilde{p}_n$. General solutions of the homogeneous equations are either a scalar or a vector harmonic field.

In the present case, that is, for $\tilde{p} = \tilde{p}_1$, the displacement field d can be expressed as (Love, 1927)

$$m\mathbf{d} = -\tilde{\mu\mathbf{u}} + \bar{A}\left(\frac{r^2}{3}\cdot\nabla\tilde{p}_1 - \tilde{p}_1\mathbf{x}\right) + \frac{\hat{\psi}_1}{6}\cdot\frac{H}{F}\cdot r^2\nabla\tilde{p}_1$$

$$-\frac{1}{4(1-N)}\cdot\nabla\left[\left(\frac{\hat{\psi}_1}{15}\cdot\frac{H}{F} - \frac{2}{3}\cdot\bar{A}\right)r^2\tilde{p}_1\right] \qquad (B3)$$

where $\bar{A}$ is determined by the boundary condition (5).

Two constants are generally necessary to determine the displacement field d (see Adler, 1978). But in the particular case of solid spherical harmonics of order 1, boundary conditions can be fulfilled with only one constant, since the total force exerted upon the porous solid matrix must be equal to the apparent weight of the porous particle.

The stress tensor is determined from (B3) and (3). Its deviatoric part is given by (9), where T is expressed as

$$T = \frac{H}{6F}\cdot(2\hat{\psi}_1 + \xi_1^2\hat{\psi}_3 - \hat{\psi}_2) \qquad (B4)$$

The coefficients which appear in the yield condition (10) are given by

$$\mathcal{L} = 2\xi^2\cdot\left(\psi_2 - \frac{\psi_1}{2} + \frac{F}{H}\cdot T\right)^2 \qquad (B5a)$$

$$\mathcal{M} = \frac{\psi_1^2}{2} + 9\psi_2^2 - 4\psi_1\psi_2 + \psi_3^2\xi^4 + 6\psi_2\psi_3\xi^2 - 2\psi_1\psi_3\xi^2 + \frac{2}{3}\cdot\frac{F}{H}\cdot T\cdot(4\psi_3\xi^2 + 2\psi_2 - \psi_1) + \frac{2}{3}\cdot\left(\frac{F}{H}\cdot T\right)^2 \qquad (B5b)$$

Manuscript received April 24, 1978; revision received January 22, and accepted February 6, 1979.

Quantitative Interpretation of Phase Volume Behavior of Multicomponent Systems Near Critical Points

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Equations describing phase volumes in multicomponent, multiphase systems in the neighborhood of critical points are derived to aid in the location of such critical points. The theory is in good agreement with experiments for three ternary systems and four surfactant systems of the type used for tertiary oil recovery.

SCOPE

The behavior of phase volumes of multicomponent systems in the neighborhood of critical points is indicative of the nearness to such points. Since interfacial tensions between the critical phases become vanishingly small near a critical point, location of critical points should prove beneficial in the design of tertiary oil recovery systems employing surfactants or high pressure gases.

A convenient way of representing the phase volumes of multicomponent systems is to employ phase volume diagrams. Such a diagram expresses the relative volumes of phases present in a series of samples whose overall compositions lie along some smooth path in the phase diagram. Modern theory of critical phenomena has been used to develop equations relating the shapes of phase volume diagrams to the proximity to critical points.