Determination of yield value of hectorite gels by the falling sphere method

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Two variations of the falling sphere method were used to measure the static yield values of aqueous dispersions of a synthetic hectorite and the results compared with those obtained using the Ferranti Shirley cone-plate viscometer. Yield values were calculated from three equations proposed by various workers but only one equation gave results in reasonable agreement with the cone-plate viscometer. Advantages of the falling sphere method and the derivation of the equations are discussed.

One of the criticisms of rotational viscometers such as the cone-plate or co-axial type for measuring the yield value of a semi-solid (Schulte & Kassem, 1963, 1964; Gohlke & Hoffman, 1967; Boylan, 1966, 1967; Talman, Davies & Rowan, 1967) is that the structure of the system may be broken down during measurement (Davis, Shotton & Warburton, 1968; Warburton & Barry, 1968). This makes the determination of yield value of thixotropic gels particularly difficult and two yield values, "static" and "dynamic" are cited to characterize such gels. The falling sphere at low rates of shear minimizes structural disturbance and may therefore be more accurate for the determination of the static yield value of thixotropic materials. However, the use of the method is made difficult by the fact that no satisfactory theory of the forces experienced by bodies immersed in plastic fluids has so far developed. Oldroyd (1947) has presented a mathematical solution to the problem of estimating the force which will just cause a knife-edge immersed in a plastic fluid to move but it has not been possible to extend the solution to other shapes. Experimental investigation by several workers (Boardman & Whitmore, 1960; Rae, 1962; Hirota & Takada, 1959; Valentik & Whitmore, 1965; Brookes & Whitmore, 1968) have not produced generally accepted results.

Equations relating static yield value with the size and density of a sphere have been reported by Schischtschenko and Baklanow:—

$$S = \frac{\Delta g \, r_0}{3} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

Meyer and Cohen (1959):

$$S = \frac{4\Delta g \, r_0}{3} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

and Williams & Fulmer (1938):

$$S = \frac{2\Delta g \, r_0{}^2}{9 \, (R-r)} f \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where S is static yield value, r_0 is the radius of the sphere which the dispersion can just

support, Δ is the density difference between the sphere and the dispersion, g is gravitational constant, R the radius of the fall vessel and f Faxen's correction factor for wall effect $= (1-2\cdot104r/R)$.

In view of the importance of static yield value to the suspending ability of dispersions, the present work was carried out to find which of these equations was most applicable to aqueous dispersions of a synthetic hectorite (Laponite CP). Two variations of the falling sphere method were used: (i) spheres of the same density but different diameter and (ii) spheres of the same diameter but different density.

Equations (1) and (2) are applicable to data obtained by either variation of the method but equation (3) is applicable only to the method employing spheres of constant diameter.

MATERIALS AND METHODS

Materials. Hectorite—Laponite CP supplied by Laporte Industries Limited. Distilled water—triple glass-distilled water; conductivity $1\cdot72$ μmhos.

Apparatus

Cone-plate viscometer. A Ferranti Shirley cone and plate viscometer was used as previously described (Carless & Ocran, 1972).

Falling sphere viscometer. This was a graduated cylinder supported vertically in a constant temperature bath at $30 \pm 0\cdot01°$. The internal diameter of each cylinder was measured with a travelling telescope.

Two groups of spheres were used: spheres of the same diameter but different densities (2–11 g cm^{-3}) and spheres of the same density but different diameter (0·3–0·7 cm). Diameters were checked in four different directions with a Mercer gauge and spheres in which any diameter differed from the mean by more than $2\cdot54 \times 10^{-3}$ cm were rejected. Density was calculated from the weight and diameter of the sphere. The density of dispersions was measured within 1 h of preparation while the dispersions were still fluid using the specific gravity bottle method.

Procedure. The tube was filled to a few mm from the top with a freshly prepared hectorite dispersion, avoiding air bubbles, and left to stand at room temperature for 24 h. Evaporation of water from the dispersion was prevented using a rubber stopper covered with filter paper soaked in 40% w/v glycerol in water. At the end of the ageing period the tube was transferred to the thermostat bath and left for 2 h for temperature equilibrium to be attained. The sphere was introduced gently on top of the gel and the time taken to travel between two marks (6·582 cm apart) in the middle two-thirds of the tube measured. The passage of the sphere was observed through a travelling telescope to avoid parallax error.

Preparation of hectorite dispersions

Hectorite dispersions were prepared as described by Carless & Ocran (1972).

Yield value measurements

The static yield values of dispersions containing different concentrations of hectorite in water were determined using both variations of the falling sphere method and also the Ferranti Shirley viscometer. In the case of the latter instrument all samples were subjected to a standard preliminary treatment (Carless and Ocran, 1972).

Table 1. *Velocity of spheres of constant density.* Hectorite concentration 4% w/v; density of dispersion 1·0215 g cm⁻³; Sphere density 7·775 g cm⁻³; container diameter 6·901 cm.

Sphere diameter (cm)	Corrected velocity (cm s⁻¹)		
	Expt. 1	Expt. 2	Expt. 3
0·674	0·1380	0·1463	0·1447
0·624	0·1022	0·1027	0·1014
0·539	0·0319	0·0289	0·0298
0·517	0·0115	0·0118	0·0106

Table 2. *Velocity of spheres of constant diameter.* Hectorite concentration 4% w/v; Density of dispersion 1·0215 g cm⁻³; Sphere diameter 0·630 ± 0·006 cm; Container diameter 6·901 cm.

Density difference (g cm⁻³)	Measured velocity (cm s⁻¹)			Corrected velocity (cm s⁻¹)		
	1	2	3	1	2	3
7·311	0·1184	0·1143	0·1150	0·1430	0·1380	0·1389
6·749	0·0819	0·9893	0·0826	0·0989	0·1079	0·0997
6·000	0·0405	0·0421	0·0429	0·0489	0·0509	0·0519
5·612	0·0189	0·0198	0·0198	0·0221	0·0239	0·0240

Table 3. *Velocity of spheres of constant density.* Hectorite concentration 3·5% w/v; Density of dispersion 1·019 g cm⁻³; Sphere density 7·775 g cm⁻³; Container diameter 6·901 cm.

Sphere diameter (cm)	Corrected velocity (cm s⁻¹)		
	1	2	3
0·552	0·0894	0·0884	0·0901
0·472	0·0725	0·0744	0·0721
0·394	0·0561	0·0562	0·0589
0·314	0·0409	0·0411	0·0431

Table 4. *Velocity of spheres of constant diameter.* Hectorite concentration 3·5% w/v; Density of dispersion 1·019 g cm⁻³; Sphere diameter 0·313 ± 0·002 cm; Container diameter 3·312 cm.

Density difference	Measured velocity (cm s⁻¹)			Corrected velocity (cm s⁻¹)		
	1	2	3	1	2	3
8·652	0·1184	0·1143	0·1150	0·1430	0·1380	0·1389
6·751	0·0819	0·0833	0·0826	0·0989	0·1034	0·0997
5·614	0·0405	0·0421	0·0429	0·0489	0·0509	0·0519
3·611	0·0181	0·0187	0·0198	0·0219	0·0229	0·0240

RESULTS AND DISCUSSION

The falling sphere method is based on Stokes' Law which gives the velocity of a sphere falling freely in a fluid contained in an infinitely large vessel.   For a sphere falling in a container of finite dimensions the motion has been found to be affected by the drag exerted by the walls.   Several equations have been proposed to account for the wall effect (Ladenburg, 1907; Faxen, 1922–23; Francis, 1933) but the generally accepted one is that of Faxen's:

$$V_\infty = \frac{V_{obs}}{1-2 \cdot 104 d/D} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

where V_∞ is the velocity of the sphere in infinite medium; V_{obs} is the observed or measured velocity: d is the sphere diameter and D the diameter of the vessel.

In this work all velocities were corrected for wall effect by applying Faxen's equation (Tables 1–4).   No correction was applied to take into account the effect of the ends of the fall vessel since the distance between the lower mark and the bottom of the vessel was greater than twice the diameter of any of the spheres (Barr, 1931).

In using spheres of the same density, sphere diameter was plotted against the corrected velocity and the resulting straight line extrapolated to zero velocity (Fig. 1A).
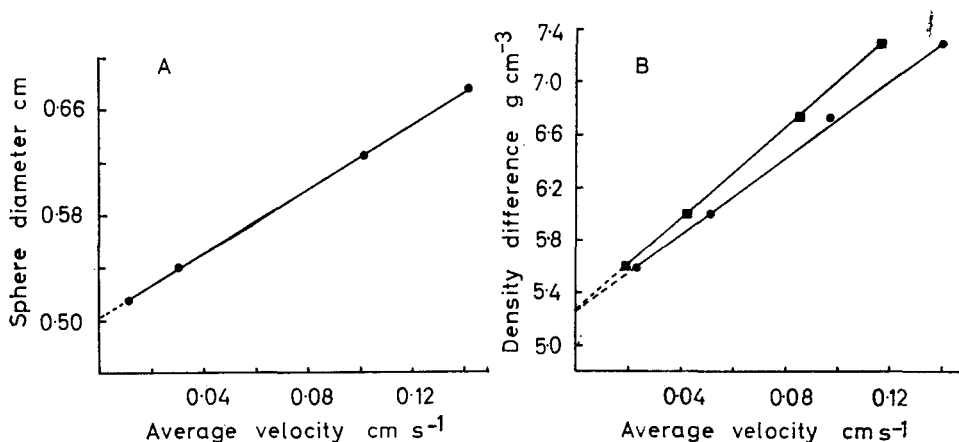

FIG. 1.   A. Yield value determination using spheres of constant density.   Plot of sphere diameter against corrected velocity.   Dispersion: 4% w/v hectorite-water.   Sphere density: 7·775 g cm⁻³.
B.   Yield value determination using spheres of constant diameter.   Plot of density difference versus velocity.   ● Measured velocity.   ■ Corrected velocity.   Dispersion =4% w/v hectorite-water.   Sphere diameter = 0·630 ± 0·006 cm.

The intercept was the diameter of the sphere of known density which could just be supported by the dispersion (i.e. 2 r_0 in equations 1–3).   When spheres of constant diameter were used, density difference (density of sphere — density of dispersion) was plotted against the corrected velocity and the line extrapolated to zero velocity to obtain Δ for use in equations 1 and 2.   In the use of equation 3 the intercept, Δ, was obtained from the plot of density difference versus measured (uncorrected) velocity (Fig. 1B).

Structural breakdown of the sample during transfer to the viscometer and adjustment of cone-plate gap makes it necessary for each sample to be subjected to a care-

fully standardized pre-treatment before a rate of shear versus shear stress curve is obtained.

In the falling sphere viscometer, measurement is made in the container in which structural build-up takes place so that the sample is undisturbed until the test is commenced. The sphere is continuously moving through fresh portions of the dispersion so that the method is more likely to give the true static yield value. Table 3 shows that of the three equations used in the present work only equation (1) (Schischt-schenko & Baklanow) gives results in reasonable agreement with those obtained from the cone-plate viscometer. The derivation of the equations will now be discussed.

The flow of Newtonian fluids is represented by the equation

$$F = \eta \, \frac{dv}{dx} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where F is the shear force per unit area, η is the viscosity and dv/dx is the rate of shear.

Bingham (1922) proposed an analogous equation for the flow of plastic fluids

$$F - S = \eta' \, \frac{dv}{dx} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

in which S is the force per unit area which must be exceeded before flow occurs (static yield value) and η' the viscosity when yield value is exceeded. In yield value measurement involving the use of spheres of the same density, the diameter at zero velocity obtained by extrapolation represents the diameter of a sphere of known density which can just be supported by the dispersion. Similarly, when using spheres of constant diameter, the density difference at zero velocity obtained by extrapolation, represents the density difference between a sphere of known size that the dispersion can just support and the dispersion. At the point where the sphere just fails to move it exerts a force equal to the static yield value, or at that point equation (6) becomes

$$F = S$$

and the intercept can therefore be used to calculate yield value. Lamb (1916) has shown that the shearing force F at the equator of a sphere moving through infinite medium of viscosity is given by

$$F = (3/2) \, \eta \, V/r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

where V is the velocity and r the radius of the sphere. Stokes derived the following equation for the velocity of a sphere of radius r and density ρ_s falling freely in infinite medium of viscosity η and density ρ_1:

$$V = \frac{2 \, r^2 \, g \, (\rho_s - \rho_1)}{9\eta} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

Substituting for V in Lamb's equation gives

$$F = \frac{g \, r(\rho_s - \rho_1)}{3} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

But, as already pointed out, at zero velocity

$$F = S$$

Therefore

$$S = \frac{r_0 \Delta g}{3} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

where r_0 is the radius of the sphere which the dispersion can just support and Δ is the difference in density between the sphere and the dispersion. Equation (10) which was proposed by Schischtschenko & Baklanow has been criticized (Williams & Fulmer, 1938) for ignoring the effect of the walls of the fall vessel on the velocity of the sphere. In our work the criticism was met by applying Faxen's equation (1922–23) to correct the velocity and using the corrected velocity to obtain r_0 or Δ. Kulakoff (1937) applied Schischtschenko & Baklanow's equation and reported that the results did not agree with those obtained from the capillary and Couette viscometers but it should be pointed out that he worked at velocities above which Stokes' equation was applicable.

The difference between equation (10) and that of Williams & Fulmer (1938) arises essentially from the uncertainty over the correct estimation of the shearing force on a sphere moving through infinite medium. In deriving their equation Schschtschenko & Baklonow made use of the expression derived by Lamb (eqn 7); Williams & Fulmer, on the other hand, considered that derived by Pasynskii & Rabinovich (1934)

$$F = \frac{V}{R-r} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11)$$

to be the right equation and hence obtained a different formula (eqn 3).

Meyer & Cohen (1959) derived equation (2) empirically by dividing the effective weight of the sphere submerged in a fluid by the cross-sectional area and compared their results with those obtained using the Brookfield viscometer. The Brookfield viscometer yield value was defined as

$$\frac{\text{(Apparent viscosity at 0·5 rev/min} - \text{Apparent viscosity at 1 rev/min)}}{100}$$

This is obviously not the same as static yield value obtained by the falling sphere method or from the cone-plate viscometer and indicates that the equation proposed by these workers cannot be accepted to give the true yield value.

The difference (approximately 10%) between static yield values obtained from the falling sphere viscometer applying equation (1) and those from the cone-plate viscometer (Table 5) is probably due to the fact that structure broken down during the pre-treatment in the latter instrument was not fully rebuilt before obtaining the flow curves.

The static yield value measured under these conditions is thus not an absolute value, but depends on the previous history of the gel. It is however, a useful comparative method.

It can be seen from Table 5 that for each particular equation, results obtained by the two variations of the falling sphere method agreed within 1% so the choice of method may be determined mainly by the size and density of the spheres available.

Table 5. *Static yield values (dynes cm^{-2}) measured by different methods.*

Dispersion	Method	Equation (1)	Equation (2)	Equation (3)	Cone-plate viscometer
4% w/v Hectorite-water	Constant density	545; 540; 542 Av: 542	2179; 2162; 2170 Av: 2170		497
,, ,,	Constant diameter	540; 540; 535 Av: 538	2161; 2161; 2140 Av: 2154	30; 30; 30 Av: 30	
3·5% w/v Hectorite-water	Constant density	121; 121; 116 Av: 119	485; 485; 463 Av: 478		109
,, ,,	Constant diameter	123; 120; 117 Av: 120	490; 480; 470 Av: 480	6·7; 6·8; 6·8 Av: 6·8	

The large static yield value of hectorite gels allows solids to remain in permanent suspension, and their rapid breakdown on shaking enables pouring of the material particularly as the rate of gel formation is not too rapid (Carless & Nixon, 1970). The falling sphere method is more suitable than the cone and plate viscometer for determining the static yield value of weak gels, i.e. gels with yield values below about 20 dyne cm^{-2}. In pharmaceutical suspensions, the yield value of a vehicle necessary to support say particles of a solid of density 1·5 g cm^{-3} and 200 μm diameter, in a vehicle of density 1·0 g cm^{-3}, would be approximately 0·3 dyne cm^{-2}. This is calculated from equation (1). Assessing yield values of this magnitude the falling sphere method would be potentially useful. Practical limitations of the method are the difficulties in obtaining spheres of suitable density in a range of sizes.

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