

# SOME OBSERVATIONS ON THE FLOW PROPERTIES OF BARIUM SULPHATE SUSPENSIONS

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Barium sulphate particles of narrow size range were prepared by precipitation and the flow properties of suspensions of these particles were investigated. Particle sizes were determined by a photo-extinction sedimentometer method. The mean size of the particles varied from  $6 \mu$  to less than  $1 \mu$ . The flow properties of the suspensions can be explained by relating the viscosity not only to the volume concentration of the solid present but also to the volume of "free liquid" in the suspension. The Roscoe equation equating the relative viscosity to the concentration of a suspension, fits the experimental results, if an "effective concentration" is substituted for the actual concentration of solid. The "effective concentration" is the total volume of solid together with the solvent trapped within clumps of particles. This effective concentration was estimated from the sedimentation volume of the suspension.

THE viscosity of a suspension is raised to a value  $\eta$  which is higher than the viscosity  $\eta_0$  of the suspending liquid alone. The ratio  $\eta/\eta_0$  is known as the relative viscosity ( $\eta_r$ ) of the suspension. The basic equation of Einstein states that the relative viscosity of a suspension is related to the concentration of the solid present expressed as a fraction of the total volume ( $c$ ):

$$\eta_r = 1 + 2.5 c$$

or  $\eta_{sp} = 2.5 c$ , where  $\eta_{sp}$  is the specific viscosity

of the suspension.

This only applies to a dilute suspension of spherical monodispersed particles. Modifications of the equation to extend its application to higher concentrations have been proposed by numerous investigators. This aspect has been reviewed by Ward (1955). In most of the reported work on viscosity-concentration relations of suspensions, the particles have been relatively large, e.g.,  $10$ – $100 \mu$ . The present paper reports a preliminary investigation of the rheological properties of barium sulphate particles below  $6 \mu$ .

## EXPERIMENTAL

### *Materials*

The method of Andreason (1943) was used to prepare spherical, mono-dispersed particles of barium sulphate. The precipitated barium sulphate was washed with deionised water, then with ethanol (95 per cent), acetone and finally dried. Suspensions of varying volume concentrations were made up using a suspending medium of 40 per cent v/v glycerol containing 0.1 per cent w/v sodium pyrophosphate.

*Methods*

A Ferranti-Shirley cone plate viscometer as described by McKennell (1954) was used to measure the flow properties. All the measurements were made at  $28^{\circ} \pm 0.1^{\circ}$ .

The particle size analyses of the powders were made using a photo-extinction sedimentometer (Evans Electroselenium Ltd.) based on a design of Rose (1958). The technique has been described by Carless and Chenoy (1961).

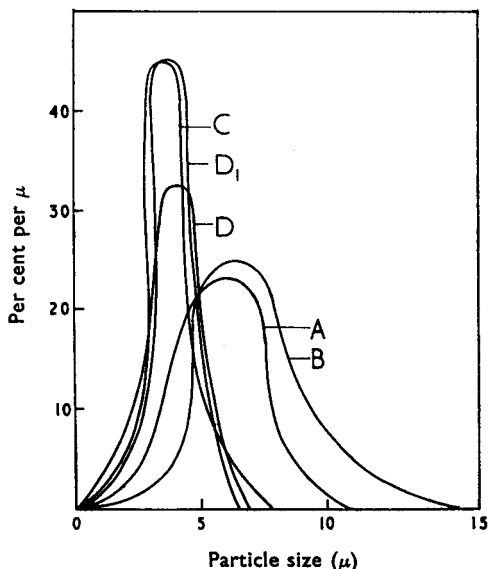


FIG. 1. Particle size distribution curves of barium sulphate powders.

The sedimentation volumes under gravity settling were determined by allowing 25 ml. of a 10 per cent v/v suspension of the sample in 0.1 per cent sodium pyrophosphate in water, to settle in a standard measuring cylinder for 7 days. The sedimentation volumes under centrifugal

TABLE I  
PHYSICAL CHARACTERISTICS OF PRECIPITATED BARIUM SULPHATE POWDERS

Sample	Mean particle size ( $\mu$ )	Shape	State of dispersion (5 per cent v/v suspension)
A	6.0	Cubical-spherical	Deflocculated
B	6.5	Spherical	Flocculated
C	3.75	"	Deflocculated
D	4.0	"	"
D <sub>1</sub>	4.0	Irregular	"
E	<0.5	—	"

settling were determined by subjecting 10 ml. of a 10 per cent v/v suspension of the sample in the suspending medium, to a force of approximately 400 g for 10 min.

## RESULTS AND DISCUSSION

The physical characteristics of the precipitated barium sulphate samples is shown in Table I, and the size distribution curves appear in Fig. 1.

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Microscopic examination of the suspensions (5 per cent v/v) was made to check that the particles were effectively deflocculated. Of all the samples, only B was observed to be flocculated.

The variation of relative viscosity ( $\eta_r$ ) with concentration ( $c$ ) is shown in Fig. 2. All concentrations are expressed as v/v. Suspensions of A, B, C, D and D<sub>1</sub> were Newtonian at all concentrations used (1–25 per cent v/v). The suspension of E was Newtonian only up to 15 per cent v/v and at greater concentrations it showed thixotropy (see Fig. 3). The thixotropy is attributed to the sample being flocculated at high concentrations

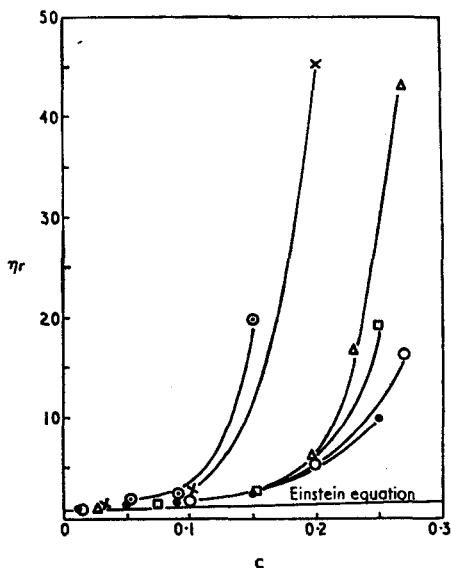


FIG. 2. Variation of relative viscosity with volume concentration.

- Sample A.    Δ Sample B.    ○ Sample C.    □ Sample D.    X Sample D<sub>1</sub>.  
 ⊙ Sample E.

which results in a gel-like structure. It is interesting to note that this anomalous flow occurred only with the finest sample of powder. Similar behaviour for glass spheres in suspension has been reported by Williams (1953). The flow behaviour of suspensions of all samples above 10 per cent concentration showed a marked divergence from the Einstein equation. The results do not fit the equations postulated by Vand (1948) to account for hydrodynamic factors or by Roscoe (1952) to account for non-uniformity of the particles, agreement becoming less with decreasing particle size. Robinson (1949) postulated that the specific viscosity ( $\eta_{sp}$ ) is not only a function of the volume concentration of the solid but is also a function of "free" liquid outside the particles or aggregates of particles. He suggested the following equation was applicable to a suspension of any concentration:

$$\eta_{sp} = \frac{Kc}{(1-Sc)}$$

Where  $c$  is the volume concentration and  $S$  the volume that a unit volume of particles would occupy when allowed to settle from a suspension. Thus  $1-Sc$  is the volume of the free liquid. The plot of  $c/\eta_{sp}$  against  $c$

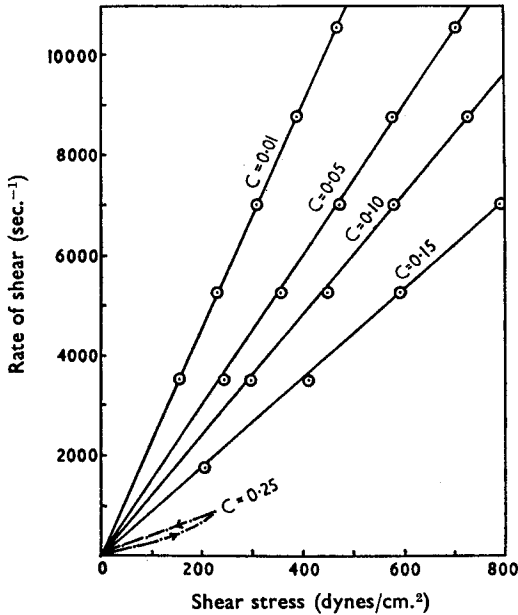


FIG. 3. Rate of shear vs. shear stress diagram for suspension of powder E.

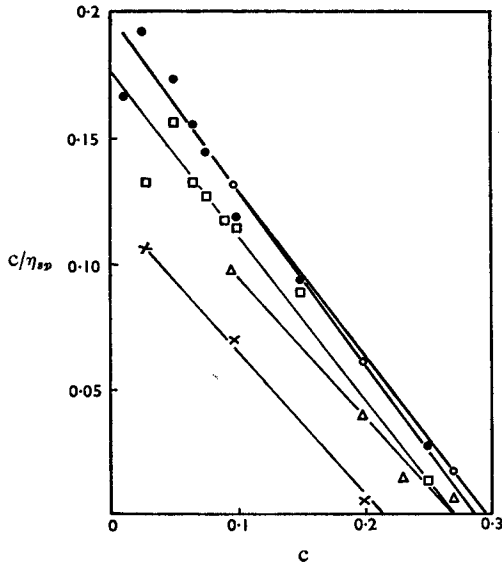


FIG. 4. Plot of  $c/\eta_{sp}$  vs.  $c$ .  
 ● Sample A.    △ Sample B.    ○ Sample C.    □ Sample D.    X Sample D<sub>1</sub>.

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should yield a straight line with the intercept on the  $c$  axis being equal to  $1/S$ . The results for A, B, C, D and  $D_1$  are shown in Fig. 4, and the predicted sedimentation volumes ( $S$ ) appear in Table II together with the observed sedimentation volumes. The results show that the predicted values of  $S$  are similar to those values obtained from sedimentation volume measurement. This agreement appears to hold for both flocculated and deflocculated suspensions.

For uniform spheres in closest packing the voidage is 26 per cent, thus the theoretical sedimentation volume per unit volume of spheres, under ideal conditions, would be 1.35. From these observations it appeared likely that the reason for the variation between  $\eta_r$  vs.  $c$  curves (Fig. 2) for different powders might be caused by variation in the "effective con-

TABLE II  
SEDIMENTATION VOLUMES OF BARIUM SULPHATE SUSPENSIONS

Sample	Sedimentation volume per unit volume of solid		
	Gravity*	Centrifuged*	$S$ from viscosity measurements
A	2.3	2.4	3.6
B	3.2	3.4	3.7
C	2.4	—	3.4
D	3.0	3.1	3.7
$D_1$	4.2	4.0	4.7

\* Concentration of suspension 10 per cent v/v.

centration" of the dispersed phase. An estimate of the effective concentration was obtained by multiplying the actual solid concentration by the ratio of the observed sedimentation volume to the theoretical sedimentation volume. Effective concentration for samples A, B, C, D and  $D_1$  together with the  $\eta_r$  values appear in Fig. 5. The line represents the Roscoe equation for uniform spheres.

$$\eta_r = (1 - 1.35 c)^{-2.5}$$

It appears therefore that all these suspensions show the same viscosity-concentration relation provided that allowance is made for the effective volume of solid.

Possible reasons for the observed sedimentation volumes being several times greater than the theoretical are: (i) immobilisation of fluid between clumps of particles; (ii) presence of an "immobilised liquid shell" around each particle.

From Fig. 2 it appears likely that flocculation is responsible for the difference in viscosity between A and B since the particle sizes are approximately the same. The structure of the aggregates is such that Newtonian flow is observed over a wide range of shear rates and concentration. Fine particles tend to aggregate to a greater extent than coarse ones so that the results in Fig. 2 are not unexpected. It is generally accepted that flocculation of particles is likely to be promoted on increasing the concentration of a suspension due to increased particle-particle contacts. In this present work the fact that the  $c/\eta_{sp}$  vs.  $c$  curve is linear, indicates that the proportion of flocculated solid to deflocculated solid remains constant over a wide concentration range.

The alternative explanation that the increased viscosity with decreased particle size is caused by an "immobilised liquid shell" would be reasonable if one assumes that the thickness of the shell is approximately the same for all particles, irrespective of size. Thus the effective volume increase would be greater for smaller particles and irregularly shaped particles. An estimate based on the observed sedimentation volumes,

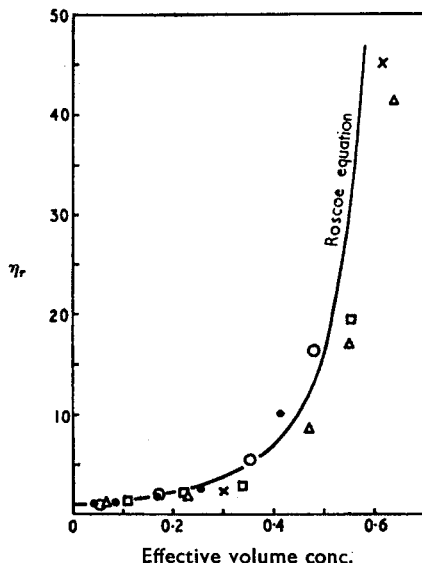


FIG. 5. Relation between relative viscosity and effective volume concentration of barium sulphate suspensions. (The line represents the Roscoe equation for uniform spheres (Roscoe, 1952).)

● Sample A. △ Sample B. ○ Sample C. □ Sample D. × Sample D<sub>1</sub>.

indicates that the shell thickness would have to be about  $1\mu$ . The Newtonian flow characteristics of the suspensions would support this explanation. However, this concept cannot explain the differences between deflocculated A and flocculated B, whose individual particles are of similar size. It appears more likely that trapping of the suspending medium between clumps of barium sulphate particles increases the concentration of the dispersed phase and this is responsible for the effects observed.

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