METHODS OF MEASURING YIELD VALUE, VISCOSITY AND THIXOTROPY*

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ABSTRACT. The capillary and the rotary viscometer do not give the same Bingham yield value and viscosity for bentonite suspensions A direct method using a rectangular flat cell for measuring the velocity gradient along the normal during flow has been developed which is expected to give yield value and viscosity in absolute units. Values obtained by the velocity gradient method are more in accord with those obtained by the rotary viscometer than those obtained by the capillary viscometer. Variations in both the lower yield value and the apparent viscosity of thixotropic suspensions with time have been observed. Compared with the apparent viscosity the lower yield value appears to give a better measure of the rate of thixotropic gelation.

Bentonite is a typical colloid system which shows most of the known anomalous viscous properties depending on the colloid content and on the p_H of the system.[1] Dilute suspensions of bentonite obey Newton's equation for viscosity. Beyond a certain concentration, which depends on the nature of the suspension, yield value appears and the suspensions cease to behave as Newtonian liquids. Thixotropy appears at a somewhat higher concentration. The purpose of the present investigation has been to evolve a suitable method for the measurement of properties such as yield value, viscosity and thixotropy in absolute units.

A large number of liquids especially concentrated colloids possess a variable viscosity[2] which changes in a complicated manner with the rate of-shear or the shearing stress. The pioneering investigations on non-Newtonian liquids of Hess,[3] Hatschek,[4] Bingham,[5] Ostwald[6] and others have recently been extended by a large number of workers.[7] A new type of non-Newtonian behaviour namely thixotropy was discovered by Miss Schalek and Szegvari[8] in 1923. In thixotropic systems the coefficient of viscosity besides being a function of the rate of shear is also a function of time.

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* Communicated by the Indian Physical Society. Figs. 5, 6 and 7 have been taken from the previous paper by the same authors.

A mathematical expression for the flow of liquids possessing yield value was first developed by Bingham[5] in the following form .

$$\frac{dv}{dz} = \mu(F - f)$$ (1)

where dv/dz is the rate of shear, F the shearing stress, f the yield value and μ the coefficient of mobility, its inverse being called the coefficient of true viscosity η. The relation is obeyed[9] by bentonite suspensions excepting at very low rates of shear.

The form of a complete consistency curve obtained with bentonite suspensions is shown in figure 1. The intercepts f_l, f_{n} and f_m on the shearing stress axis are
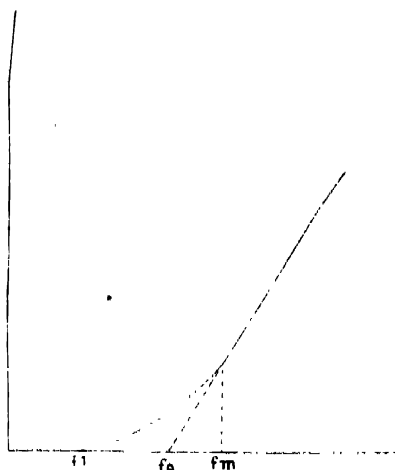

Fig 1

respectively the lower yield value, the Bingham yield value and the maximum yield value. The lower yield value is the minimum shearing stress at which the flow of a suspension begins in a viscometer. The Bingham yield value, f_n, equals the intercept on the shearing stress axis made by the straight portion of the consistency curve on extrapolation. The maximum yield value is the shearing stress above which the consistency curve becomes straight. At very low rates of shear the curve is convex towards the axis representing shearing stress and this form has been ascribed to plug flow.[10]

Ostwald[6] assumed that in the case of colloids like gelatin a structure exists in the undisturbed sol which is progressively broken down as the rate of shear is increased, so that the fluidity of the system gradually increases, i.e., the viscosity decreases.

According to Ostwald,[6]

$$dv/dz = F^n/\eta'$$ (2)

where n is a constant greater than unity and has been called the 'coefficient of structure' and η' is a constant whose dimensions are different from those of η.

Systems possessing a yield value have been called ' plastic ' and those which obey Ostwald's relation ' structure-viscous.' Many examples of both structure-viscous and plastic systems will be found in the literature while some systems show more complex behaviour.

In the usual viscometric measurements, especially by the capillary method, the rate of shear varies over a wide limit from zero at the axis to a maximum at the walls and the quantities observed represent a summation of these variations. This makes it often difficult to interpret the results since in the case of non-Newtonian liquids the ratio, shearing stress/rate of shear, is not a constant quantity and it appears that this difficulty has been the source of some controversies.[11] In view of this it is desirable that viscous properties in such systems should be estimated by direct measurements of the velocity gradient.

Complete consistency curves cannot be obtained with thixotropic systems, especially quick-gelling ones. It is, however, possible to measure the variations in apparent viscosity*[12] or lower yield value with time during thixotropic gelation. In order that the results of apparent viscosity measurements can be interpreted it is desirable that the measurements should be made at constant rates of shear. The variation of the lower yield value which gives some measure of the 'gel strength ' seems to give a better estimate of the rate of thixotropic gelation.

<center>EXPERIMENTAL</center>

Methods of preparing samples have been described elsewhere.[1] Fine subtractions of bentonites have been obtained by means of a Sharple's supercentrifuge. Hydrogen bentonites have been prepared by electrodialysis.

Consistency curves have been obtained with a capillary viscometer of the Ubbelohde type and a rotary viscometer of the Couette type which was made in
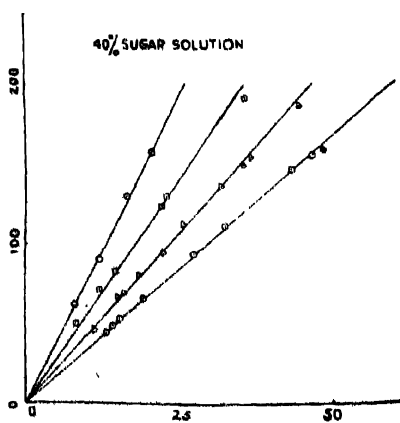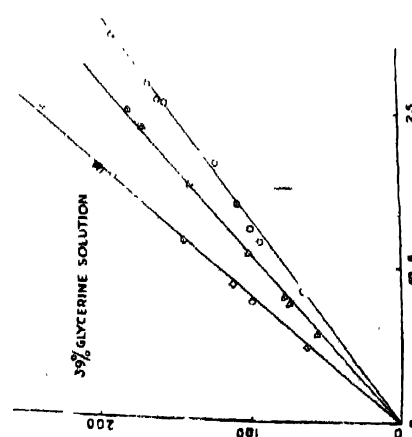

FIG. 2   FIG. 3

* Apparent viscosity is the ratio of any shearing stress and the corresponding rate of shear.

our workshop and has been described elsewhere.[13] The end correction of the viscometer has been estimated by the method of Searle.[14] Results are given in figures 2, 3 and 4. The viscosity of 40% sugar solution, corrected for end effect,
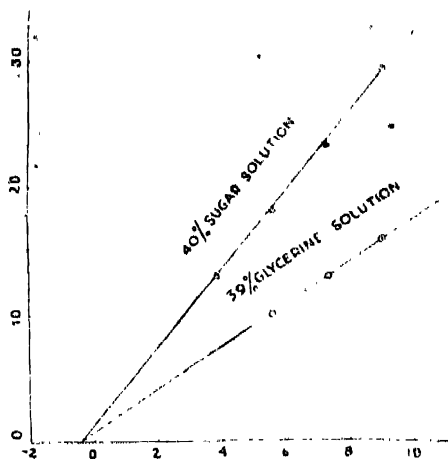

FIG. 4

is given in Table I. The corrected value agrees within 2 p.c. with the standard data. No thermostat was used and a better agreement could not be expected.

TABLE I

Length of the inner cylinder dipping into the solution	40% sugar soution η (centipoise)	
	obs.	corr.
3.85 cms.	5.14	4.55
5.6 ,,	4.96	4 55
7.35 ,,	4 85	4.54
9.1 ,,	4.90	4.75
		Mean 4 60
		From standard data 4 56*

* Barr, A Monograph on Viscometry, 1931, p. 308

The capillary viscometer has also been calibrated with the 40% sugar solution.

Lower yield values of thixotropic suspensions were measured by means of cylinders of different radii and also by a Stormer viscometer.

The procedure used in measuring the velocity gradient during flow has been described elsewhere.[15] A flat cell is used for the purpose.

Velocity gradients have been measured recently by Kroepelin,[16] Pichot[17] and Philippoff[18] for the purpose of studying viscous properties of non-Newtonian liquids. The methods used by Pichot and Philippoff do not give yield values or consistencies in absolute units. Further, as Richardson[19] has pointed out, from the two photographs published by Pichot it is difficult to distinguish between the two types of flow found in water and gelatin. The method of Kroepelin requires that the velocities should be measured at high rates of shear, at which non-Newtonian behaviour in the majority of cases is known to disappear.

In the present investigation velocities at different depths have been measured in absolute units by means of a microscope. Finely ground pure sugar charcoal has been suspended in the systems and the speeds of these particles have been measured by means of a microscope. The following systems have been used for the preliminary measurements : (a) a saturated sugar solution, (b) a gelatin sol and (c) a 2.34% hydrogen bentonite suspension consisting of very fine particles (diameter of particles 0.05—0.025μ).

RESULTS AND DISCUSSIONS

(a) Velocity gradient method

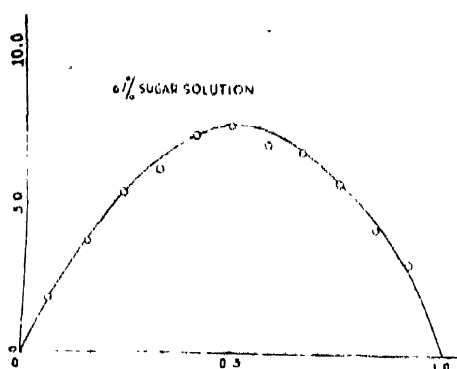Results of velocity gradient measurements are given in figures 5, 6 and 7.
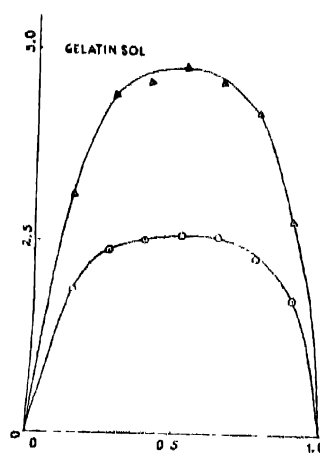

FIG. 5

FIG. 6

Figure 5 is a typical parabola. This is expected of Newtonian liquids. The pressure gradient was very small and consequently could not be measured very accurately with the present arrangement. The coefficient of viscosity obtained from the approximate pressure gradient is about 2 poise. The viscosity of the same solution measured by the rotary viscometer is 1.7 poise.

Figure 6 gives curves which are of a higher degree than the parabola. The system appears to follow Ostwald's relation (equation 2) and the value of ' n ' calculated from the two curves is approximately 2.8.

The bentonite suspensions give a parabolic curve of distribution of velocities with depth excepting the central portion which is straight and whose length
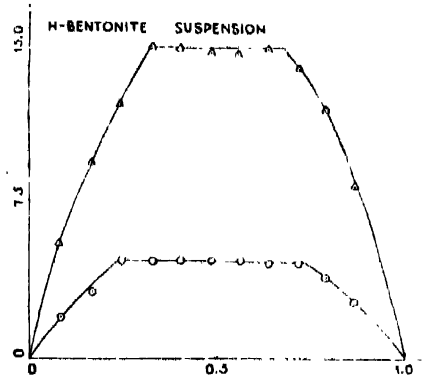

FIG. 7

diminishes at higher rates of shear. The flat portion gives a measure of the yield value of the suspension. The two curves show that the yield values are 27 and 30 dynes/sq.cm. respectively. The yield value of the same suspension obtained by the capillary viscometer is about 88 dynes/sq.cm. or about three times the value obtained by the velocity gradient method.

Further measurements by the velocity gradient method are under way.

(b) *Comparative study of the rotary viscometer and the capillary viscometer*

Consistency curves of suspensions of natural bentonites No. D_5' at concentrations of 5.0, 4.5, 4.0, 3.5 and 3.0 gms. per 100 c.c. have been obtained by the rotary and the capillary viscometers (figures 8 and 9). The curves obtained by both methods are similar in form. At the lowest concentration studied the
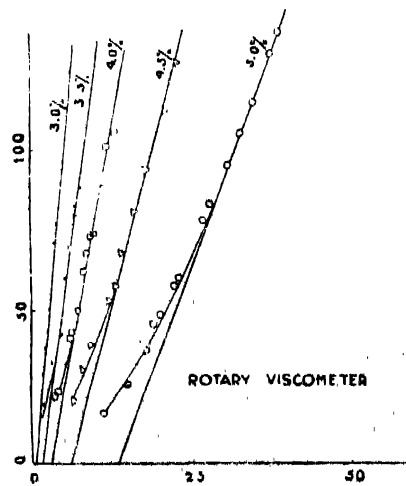

FIG. 8

curves are straight and on extrapolation pass almost through the origin. At higher concentrations the curves have a shape similar to that given in figure 1,
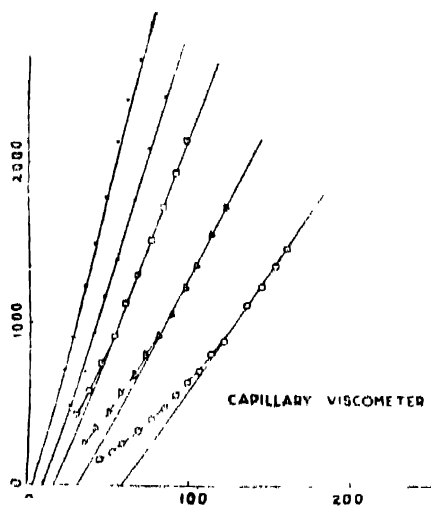

FIG. 9

The yield value and true viscosity obtained by the two methods (Table II) are different.

TABLE II

D_5' (Natural)

Concentration gms. per 100 c.c.	Yield value (dynes/sq cm)		η (centipoise)	
	Rotary	Capillary	Rotary	Capillary
5.0	13 5	58	22 2	9.0
4 5	6.0	3 3	14 3	6 6
4.0	2.5	16	10.6	4.6
3.5	1.0	8	7 6	3 5
3.0	0 2	1	5 1	2.6

The viscosities obtained by the capillary method are less than half the values obtained by the rotary method. This may be due to the wall effect in the capillary. Schofield and Scott-Blair[20] found that the mobility μ of clay suspensions diminishes with increase in the radius of the capillary. They estimated the true mobility from the consistency curves obtained by using capillaries of different radii. The mobility μ was plotted against $1/r$ where r is the radius of the capillary and the true mobility was noted from the graph by extrapolation

to $1/r=0$. In one case μ was found to be about 20 rhe for $r=0.05$ cm. and μ_0 was about half being about 10 rhe. In other words the extrapolated value of the viscosity was approximately double that for $r=0.05$ cm. This observation possibly explains the discrepancy between the true viscosities observed by us when measured by the two methods discussed here.

The yield value obtained by the capillary viscometer is about four to five times as great as that obtained by the rotary viscometer. The reason for this discrepancy is not very clear. The velocity gradient method gives values in better agreement with the rotary viscometer and the latter appears to be preferable for ordinary measurements.

The yield value and the true viscosity obtained by the two methods have been plotted against concentration in figure 10. In spite of the differences in
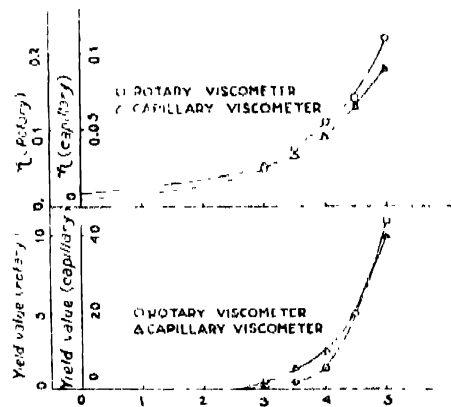

Fig. 10

magnitudes, the relative variations of viscosity and yield value given by the two methods are more or less the same and both methods seem to be equally applicable for relative measurements. This is important in practice, especially in respect of drilling mud control.

(c) *Variation of lower yield value of thixotropic suspensions with time*

The wall stress F_w in a cylinder is given by the relation $F_w = g.\rho.r/2$. ... (3)

where ρ is the specific gravity of the suspension, g the acceleration due to gravity and r the radius of the cylinder in cms. It is difficult to measure ρ for quick-gelling systems. Approximate figures are, however, sufficient for present purposes.

If t_1 is the time in seconds required for a suspension to solidify in a cylinder of radius r_1 then the lower yield value at time t_1 is $g.\rho.r_1/2$.

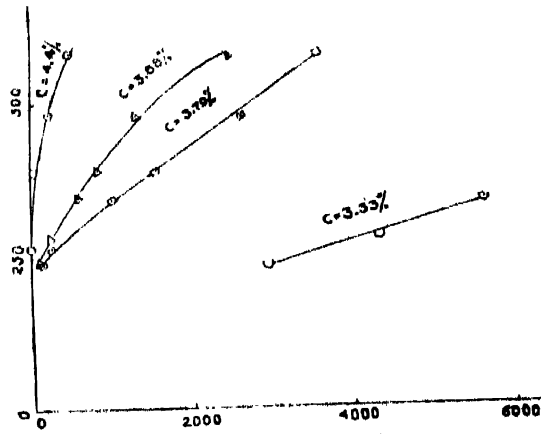Results are given in figures 11, 12 and 13 and in table III.

FIG. 11

FIG. 12

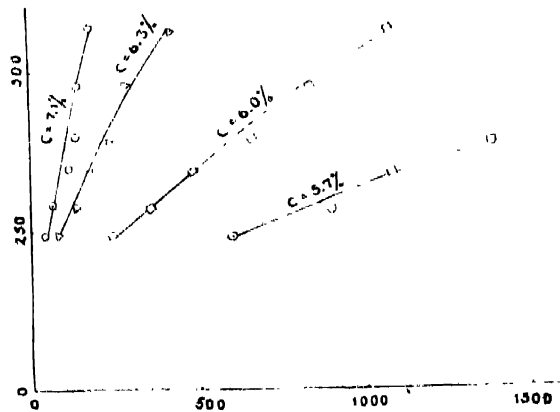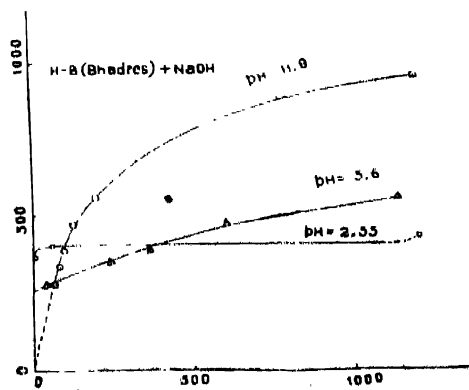FIG. 13

TABLE III

H-B + NaOH p_H-11.8 Concentration-6.0% Temperature 23-24°C

Radius of the cylinder (cm.)	Time of solidification 'seconds)	Yield value (dynes/sq.cm.)
0.48	10	242
0.56	65	283
0 68	80	343
0.77	90	389
0 94	120	474
1 11	195	560
1.83	1200	949

The lower yield value of the fine subfractions of natural bentonites (Figs. 11 and 12) increases almost linearly with time during the period of measurement. Figure 13 shows that hydrogen bentonite possesses a high initial f_l which increases only slowly with time   In the case of bentonite treated with excess of caustic soda (p_H 11.8), however, initial f_l is very small but increases rapidly with time towards a constant limiting value. At p_H 5.6 an intermediate behaviour is observed. The suspension possesses a high f_l in the thoroughly stirred condition which also increases rapidly with the period of rest to a constant limiting value. The rate of thixotropic gelation is thus strongly influenced by the p_H, a fact which does not seem to have been observed by previous workers.

TABLE IV

H-B + NaOH p_H-11.8   Temperature 23-24°C

	Concentration 6 3%		Concentration 5.3%	
Time of solidification (seconds)	Relative yield value (gms.)	Time of soldification (seconds)	Relative yield value (gms.)
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90	39.4	1140	23.1
190	37.2	1440	26.2
300	52.5	1920	29.2
660	63.3	2 20	32 6
1560	75.2	5400	35.1
0 (graph)	4 2	0 (graph)	1 0

Variation in f_t with time observed with the Stormer viscometer has been given in table IV. The yield values are not expressed in absolute but in arbitrary units. They are given in grams. Yield values at zero time have been observed from the weight/speed curve measured after shaking the sol thoroughly (Fig. 14).
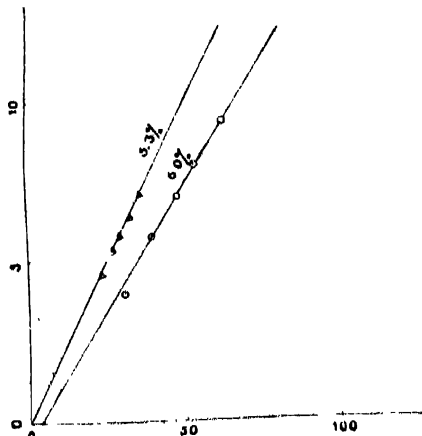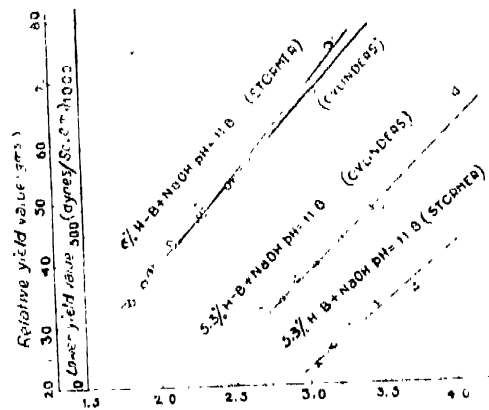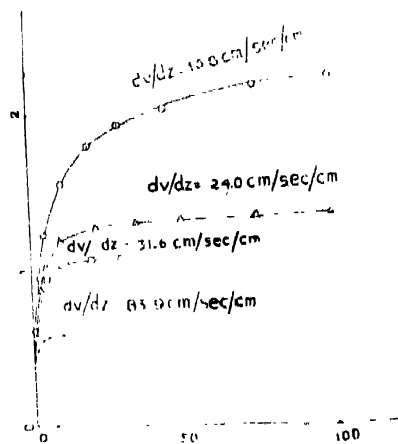

FIG. 14

FIG. 15

FIG. 16

Values of f_t are plotted against t, in figure 15. Both methods give straight lines within the range of experimental error for mixtures of different concentrations of H-B and NaOH having p_H 11.8.

(d) *Variation of the apparent viscosity η_s with time*

Variations in η_s of a thixotropic sodium bentonite suspension with time have been measured using the rotary viscometer. The rates of shear were maintained constant in each measurement. The sol was thoroughly stirred prior to each measurement. Results are given in figure 16.

η_A increases with time and finally attains a constant limiting value. This limiting value of η_A depends on the rate of shear. The higher the rate of shear the lower the limiting value of η_A and the more quickly is it reached.

R E F E R E N C E S

[1] Mukherjee, Sen Gupta and Indra, paper to be communicated shortly.

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[4] Hatschek, " The Viscosity of Liquids," Bell and Sons (1928).

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[8] Miss Schalek and Szegvari, *Kolloid-Z*, 32, 318 (1923); *Ibid.*, 33, 326 (1923).

[9] Houwink, " Elasticity, Plasticity and Structure of Matter," 345 (1937).

[10] *Ibid.*, 347 (1937).

[11] Ostwald, *Kolloid-Z*, 47, 176 (1929); Scott Blair, *Kolloid-Z.*, 47, 76 (1929); Ostwald and Auerbach, *Kolloid-Z.*, 88, 273 (1926). The phenomenon of structure viscosity has been termed *flow elasticity* by Freundlich.

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[13] Mukherjee and Sen Gupta, paper communicated to *Indian Journal of Physics.*

[14] Searle, *Proc. Cambridge Phil. Soc.*, 16, 600 (1912).

[15] Mukherjee and Sen Gupta, paper communicated to *Indian Journal of Physics.*

[16] Kroepelin, *Z. physik. Chem.*, 149, 291 (1930).

[17] Pichot, *Physics*, 5, 200 (1934).

[18] Philippoff, *Kolloid-Z.*, 83, 163 (1938).

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