Analysis of Non-Newtonian Flow by Falling-Sphere Method

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Thixotropic solution must be handled without any strong agitation in order to obtain so-called "virgin-state viscosity". Neither the capillary nor the rotating cylinder viscometer is suitable for this purpose, while the falling-sphere method is applicable, because (a) the agitation of the sample in this measunement is far less compared with that in other methods, and (b) the sphere always falls contacting with a new, so-called "virgin-state" solution.

In order to devise the falling-sphere method for this purpose it is necessary to obtain general flow curves by this method because the fluidity of these solutions normally shows shear dependence as well as time dependence.

Shear stress S_R at the equator of a sphere was given[1] by

$$S_R = R\Delta\rho g/3 \qquad (1)$$

where R is the radius of the sphere and $\Delta\rho$ is the density difference between sphere and fluid. Eq. 1 was later proved to be applicable also to non-Newtonian flow. And a necessary shear stress could be obtained by selecting a sphere of suitable radius.

For Newtonian flow, the shear rate at the equator of the sphere $(\mathrm{d}u/\mathrm{d}r)_R$ followed immediately from Stokes' equation.

$$(\mathrm{d}u/\mathrm{d}r)_R = 3U_0/2R \qquad (2)$$

Sheppard[2], however, pointed out that Eq. 2 fails to express the true shear rate in a non-Newtonian nitrocellulose solution. Phipps[3] claimed the necessity of non-Newtonian correction for Eq. 2. Many attempts[4-9] have been made to utilize the falling-sphere method for non-Newtonian systems without success establishing the corrected equation for Eq. 2 so far. The aim of this paper is to find it and to examine its applicability.

In the previous study[10] we obtained empirically

$$(\mathrm{d}u/\mathrm{d}r)_R = (3U_0/2R) \times [1 + 2.4(\mathrm{d}\log U_0/\mathrm{d}\log R - 2)] \qquad (3)$$

adopting the capillary viscometer method as the standard for which a standardized treatment of data had been proposed by Krieger and Maron[11]. In the present study, a similar result has been obtained theoretically.

Theoretical

In Newtonian Flow. — Consider a steady flow around a sphere of radius R falling

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2) S. E. Sheppard, *J. Ind. Eng. Chem.*, **9**, 523 (1917).
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11) I. M. Krieger and S. H. Maron, *J. Appl. Phys.*, **25**, 72 (1954).

slowly at the velocity U_0 in a Newtonian fluid. The rate of flow U at the distance r from the center is given[12] by

$$U = -R^3 \Delta\rho g(3+R^2/r^2)\phi/18r \qquad (4)$$

Where ϕ = fluidity = 1/viscosity

Differentiating Eq. 4 by r, we obtain the shear rate.

$$du/dr = R^3 \Delta\rho g(1+R^2/r^2)\phi/6r^2 \qquad (5)$$

Shear stress S is then

$$S = (du/dr)/\phi = R^3 \Delta\rho g(1+R^2/r^2)/6r^2 \qquad (6)$$

At $r=R$, Eq. 6 becomes Eq. 1. Eq. 1 has also been obtained directly from the calculation based on the balance between shear force and gravity without being confined to the Newtonian flow[9]. And Eq. 1 is also applicable to the non-Newtonian flow.

In Non-Newtonian Flow. — Non-Newtonian fluidity $P(S)$ is a function of S. Since the latter is a function of R and r, $P(S)$ may be regarded as a function of R and r.

$$(du/dr)/S \equiv P(S) = F(R, r) \qquad (7)$$

If we assume that only the shear rate is responsible for the non-Newtonian anomaly, and that Eq. 6 is still applicable* to the non-Newtonian flow, we may introduce Eq. 6 into Eq. 7.

$$du/dr = R^3 \Delta\rho g(1+R^2/r^2)\cdot F(R, r)/6r^2 \qquad (8)$$

Though the form of $F(R, r)$ or du/dr is unknown, the following functional equation holds.

$$U_0 = \int_R^\infty (du/dr)dr = \int_R^\infty R^3 \Delta\rho g(1+R^2/r^2) \times F(R, r)/6r^2\cdot dr \qquad (9)$$

Since non-Newtonian fluidity increases with increasing S in many cases, it increases with increasing R and decreases with increasing r. Therefore, if we assume

$$P(S) \equiv F(R, r) = f(R)\cdot g(r) \qquad (10)$$

$f(R)$ is an increasing function of R and $g(r)$ is a decreasing function of r.

Defining apparent fluidity, F_a, analogous to Stokes' equation, as

$$F_a = 9U_0/2R^2 \Delta\rho g \qquad (11)$$

and substituting Eqs. 10 and 11 into Eq. 9, we obtain

$$4F_a/3R^3\cdot f(R) = (1/R^2)\cdot\int_R^\infty g(r)/r^4\cdot dr + \int_R^\infty g(r)/r^4\cdot dr \qquad (12)$$

12) Derived from, for example, B. Fujimoto, "Ōyō Ryutairikigaku (Applied Fluid Dynamics)", Maruzen Co., Ltd., Tokyo (1941), p. 340.

which may be differentiated by R to become

$$2F_a/3R\cdot f(R)\cdot[(d\log F_a/d\log R) - (d\log f(R)/d\log R) - 3] = -g(R)/R - \int_R^\infty g(r)/r^2\cdot dr \qquad (13)$$

At $r=R$, since $F(R, R) \propto F_a$**

$$d\log F(R, R)/d\log R = d\log F_a/d\log R = H \qquad (14)$$

From Eq. 10

$$\log F(R, R) = \log f(R) + \log g(R) \qquad (15)$$

$$H = (d\log f(R)/d\log R) + G \qquad (16)$$

where

$$G = d\log g(R)/d\log R \qquad (17)$$

Introducing Eq. 16 into Eq. 13 and differentiating it again by R

$$F(R, R) = 2F_a[(G-1)(G-3) + dG/d\log R]/3(2-G) \qquad (18)$$

From Eq. 10

$$(\partial\log P(S)/\partial\log r)_R = (d\log P(S)/d\log S)\cdot(\partial\log S/\partial\log r)_R = d\log g(r)/d\log r \qquad (19)$$

where, from Eq. 6

$$\partial\log S/\partial\log r = [2r^2/(r^2+R^2)] - 4 = -3 \quad (\text{at } r=R) \qquad (20)$$

and from Eq. 1, $d\log S_R = d\log R$, then

$$d\log P(S)/d\log S = d\log F(R, R)/d\log R = H \qquad (21)$$

$$d\log g(r)/d\log r = d\log g(R)/d\log R = G \qquad (22)$$

Substituting Eqs. 20—22 into Eq. 19,

$$\left.\begin{aligned} G &= -3H \\ dG &= -3dH \end{aligned}\right\} \qquad (23)$$

Thus, Eq. 18 becomes

$$F(R, R) = F_a(1+4H+3H^2 - dH/d\log R) \times[1-(3H/2)+(3H/2)^2\cdots\cdots] \qquad (24)$$

There is an empirical fact that, for many non-Newtonian fluids, the slope of a plot of $\log F_a$ vs. $\log R$ is constant over a wide range of shear stress and is usually small as compared with unity. For example, H=0.143 in 1% NaCMC aq. (MW.=8×10^4, Deg.Eth.=0.654) as in Fig. 1.

* Discussion on the applicability will be given in another paper.

** This proportionality follows from Krieger-Maron's relation, $P(S)=F_a[1+\Delta(S)]$, where $\Delta(S)$ has been known to be constant over a wide range of S[11].

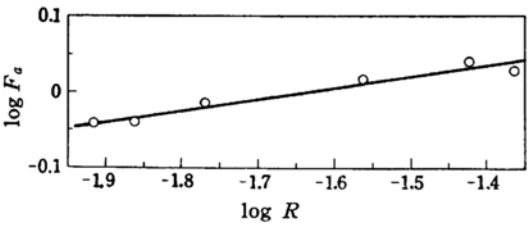

Fig. 1. Plot of $\log F_a$ vs. $\log R$ for 1% NaCMC. aq. (MW.$=8\times10^4$, Deg. Eth.$=$0.654) by falling sphere method at 25°C.

Thus,

$$\left.\begin{array}{l} d\log F_a/d\log R=H=\text{const.}<1 \\ dH/d\log R=0,\ H^3\fallingdotseq0,\ H^4\fallingdotseq0,\cdots \end{array}\right\} \quad (25)$$

Substituting Eq. 25 into Eq. 24, we have

$$F(R,R)\fallingdotseq F_a[1+2.5(d\log F_a/d\log S_R) - (3/4)(d\log F_a/d\log S_R)^2] \quad (26)$$

or

$$(du/dr)_R\fallingdotseq(3U_0/2R) \times[1+2.5(d\log U_0/d\log R-2) - (3/4)(d\log U_0/d\log R-2)^2] \quad (27)$$

which agrees very well with the empirical equation (Eq. 3).

Now, using Eqs. 1 and 27, we can obtain the exact flow curve, and hence the true viscosity by the falling-sphere method.

Experimental

For the measurement a glass tube about 20 cm. long and of 2.0 cm. in inside diameter was used, fixed in a thermostat regulated to 25±0.1°C. Glass spheres were made in the manner reported previously[10]. The fall of the sphere (density 2.50) was measured by a stop-watch over a definite distance in the sample. From these data, S_R and $(du/dr)_R$ were calculated by means of Eqs. 1 and 27. Table I gives some examples of data and calculations. Values of $d\log F_a/d\log R$ in Table I were obtained from the slope in Fig. 1. The resulting flow curve is shown in Fig. 2.

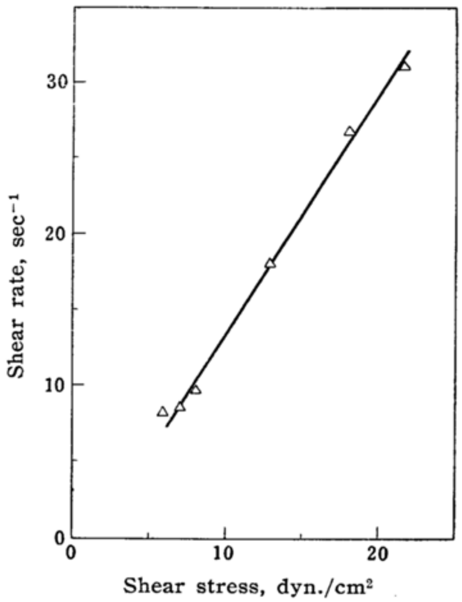

Fig. 2. Flow curve for 1% NaCMC. aq. (MW. 8×10^4, Deg. Eth. 0.654) by falling sphere method at 25°C.

TABLE I. FALLING-SPHERE METHOD. DATA AND SAMPLE CALCULATIONS FOR 1% NaCMC. aq. (MW.$=8\times10^4$, Deg. E.$=$0.654) AT 25°C

$R\times10^2$	cm.	4.35	3.78	2.74	1.70	1.37	1.21
S_R Eq. 1	dyn./cm^2	21.35	18.5	13.4	8.36	6.72	5.95
U_0	cm./sec.	0.666	0.515	0.250	0.0913	0.0558	0.0435
F_a	l./pois.	1.071	1.10	1.04	0.963	0.908	0.904
$\log F_a$		0.030	0.041	0.017	−0.016	−0.042	−0.044
$\log R$		−1.363	−1.423	−1.563	−1.769	−1.863	−1.917
$d\log F_a/d\log R$		0.143	0.143	0.143	0.143	0.143	0.143
$(du/dr)_R$ Eq. 27	1/sec.	31.2	27.8	18.6	10.9	8.26	7.30

TABLE II. SAMPLES USED FOR THE EXPERIMENT (Fig. 3)

No.	Solution	Mol. wt.	Deg. eth.	Concn., %
I	Methylcellulose aq.		0.654	1.0
II	NaCMC. aq.	8×10^4	0.654	1.0
III	NaCMC. aq.	8×10^4	0.301	1.0
IV	NaCMC. aq.	$(10\sim12)\times10^4$	0.649	1.0
V	NaCMC. aq.	8×10^4	0.654	1.2
VI	Nitrocellulose in butylacetate			12.0

Results

From Fig. 3 it is seen that the flow curves from the proposed falling-sphere method coincide very well with those from Krieger and Maron's capillary method. The difference between the empirical equation (Eq. 3) and the theoretical one (Eq. 27) is also negligibly small. These results seem to indicate the validity of our formula.

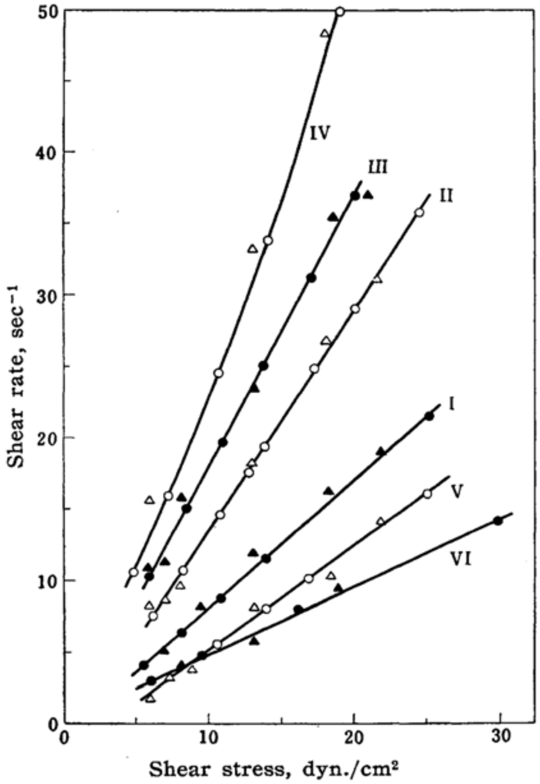

Fig. 3. Flow curves for samples in Table II at 25°C.
Falling sphere method……▲△
Capillary method …………●○

Summary

A procedure to obtain a general flow curve by falling-sphere method is presented. The shear stress S_R and shear rate $(du/dr)_R$ at the equator of the sphere are given as

$$S_R = R\Delta\rho g/3$$

$$(du/dr)_R = (3U_0/2R) \times [1+2.5(d\log U_0/d\log R-2) - (3/4)(d\log U_0/d\log R-2)^2]$$

where $\Delta\rho$ is the density difference between sphere and fluid, R the radius and U_0 the falling velocity of the sphere.

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