


Rheology

Dr. Shashi Kiran Misra

NON-NEWTONIAN SYSTEMS

- Do not follow the simple Newtonian relationship i.e., when F is plotted against G the rheogram is not a straight line passing through the origin i.e., viscosity is not a constant value.

- Such as colloidal dispersions, concentrated emulsions and suspensions, ointments, creams, gels, etc.

- These rheograms represents three types of flow:

1. Plastic
2. Pseudoplastic
3. Dilatant.

1. Plastic Flow:

Such materials are called Bingham bodies

- The curve is linear over most of its length corresponding to that of a Newtonian fluid.
- However, the curve does not pass through the origin but rather intersects the shearing stress axis (or will if the straight part of the curve is extrapolated to the axis) at a particular point referred to as the *Yield value* or *Bingham Yield value.*

- Contrary to a Newtonian liquid that flows under the slightest force, a Bingham body does not flow until a definite shearing stress equal to the yield value is applied.
- Below the yield value the system acts as an elastic material.
- Plastic systems resembles Newtonian systems at shear stresses above the yield value.
- The slope of the rheogram is termed mobility, analogous to fluidity in Newtonian systems and its reciprocal is known as the *Plastic viscosity*, U.

$$U = \frac{(F - f)}{G}$$

- Plastic flow is associated with the presence of **flocculated particles in concentrated suspensions,** however ointments and creams are common examples for that system.

- A yield value exists because of the contacts between adjacent particles (brought about by van der Waals forces), which must be broken down before flow can occur.

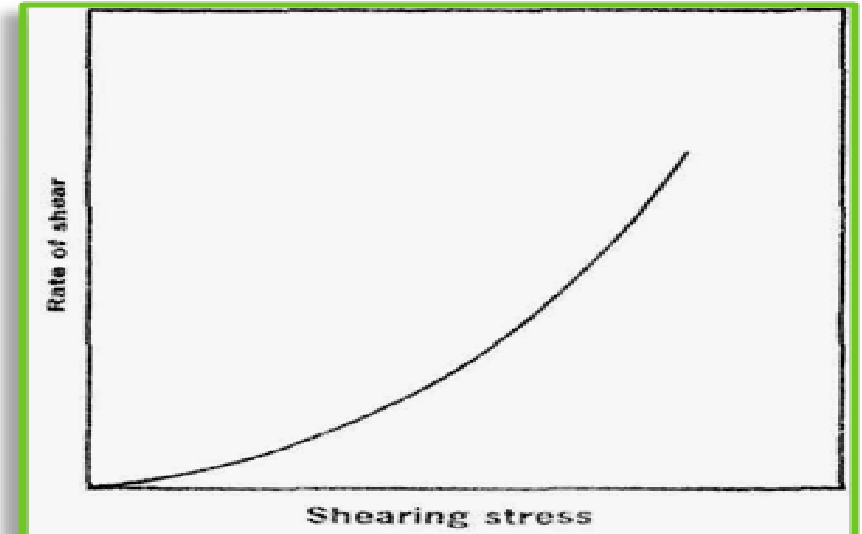
- Consequently, the yield value is an indication of force of flocculation: The more flocculated suspension, the higher will be the yield value.

- Plastic systems are **shear-thinning systems**

2. Pseudoplastic Flow:

- A large number of pharmaceutical products, including natural and synthetic gums, e.g., liquid dispersions of tragacanth, sodium alginate, methyl cellulose, and Na CMC show pseudoplastic flow.

- As a general rule pseudoplastic flow is exhibited by **polymers in solution**, in contrast to plastic systems which are composed of flocculated particles in suspension



(c) Simple pseudoplastic flow

- Curve for a pseudoplastic material begins at the origin consequently, in contrast to Bingham bodies, there is no yield value.

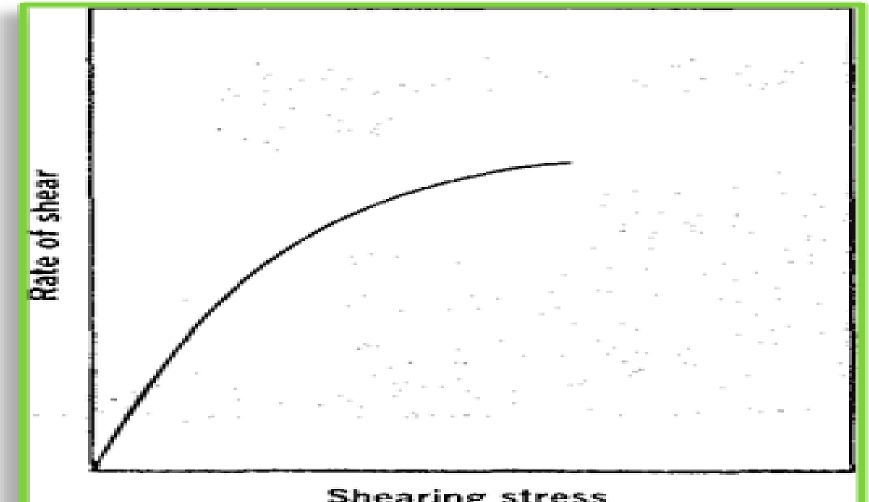
- Since no part of the curve is linear, one can not express the viscosity of a pseudoplastic material by any single value.

- The viscosity of a pseudoplastic substance decreases with increasing rate of shear (**shear-thinning systems**).

- As the shearing stress is increased, the normally-disarranged molecules begin to align their long axes in the direction of flow.

3. Dialatant Flow:

- Dilatant systems exhibit an increase in resistance to flow (viscosity) with increasing rates of shear, **"shear thickening systems".**
- Such systems actually increase in volume when sheared and are hence termed dialatant. When the stress is removed, a dialatant system returns to its original state of fluidity.



(d) Dilatant flow

- Dilatant flow is the reverse of that possessed by pseudoplastic systems.
- Substances possessing dilatant flow properties are invariably **suspensions** containing a high concentration (about 50 percent or greater) **of small, deflocculated particles.**
- Particulate systems of this type which are **flocculated** would be expected to possess **plastic,** rather than dilatant flow characteristics.

Dilatant behavior may be explained as follows:

- **At rest**, the particles are closely packed with the interparticle volume, or voids being at a minimum.

- The amount of vehicle in the suspension is sufficient, however, to fill this volume and permits the particles to move relative to one another at low rates of shear.

- Thus, one may pour a dilatant suspension from a bottle since under these conditions it is reasonably fluid.

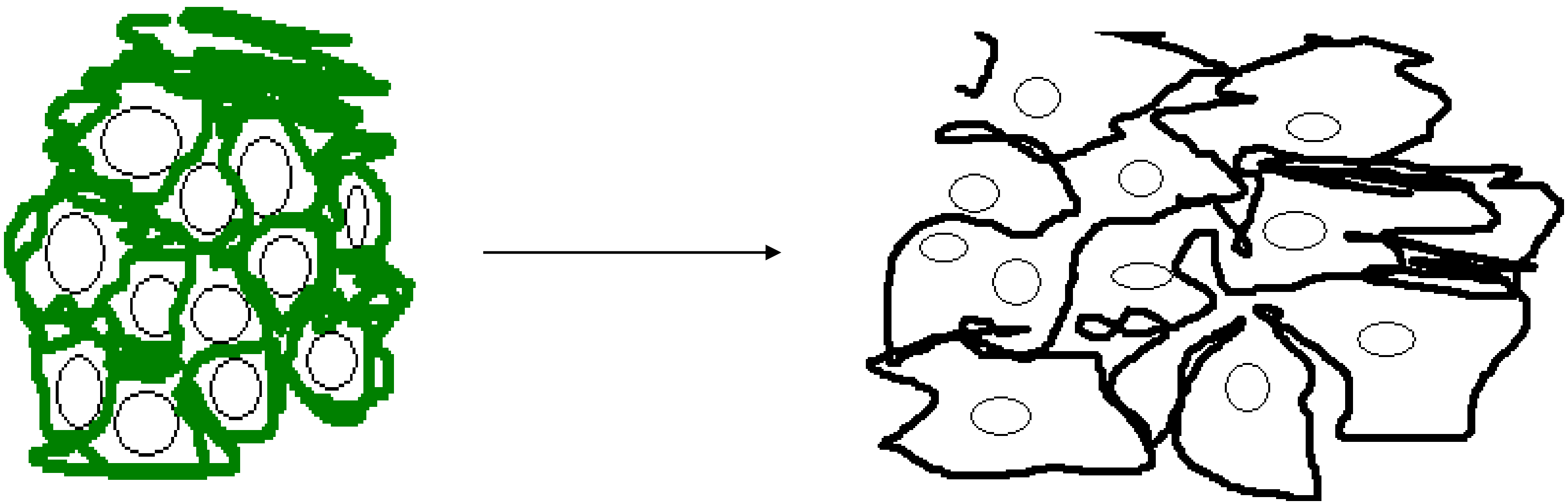
- As the shear stress is increased, the bulk of the system expands or dilates, hence the term dilatant.

- The particles, in an attempt to move quickly past each other, take on an open form of packing. Such an arrangement leads to a significant increase in the interparticle void volume.

- The amount of vehicle remains constant and at some point, becomes insufficient to fill the increased voids between the particles.

- Accordingly, the resistance to flow increases because the particles are no longer completely wetted or lubricated by the vehicle.

- Thus, the suspension will set up as a firm paste.



Closed packed particles
minimum void volume
sufficient vehicle
low viscosity

open packed particles
increase void volume
insufficient vehicle
high viscosity

Determination of Rheological Properties

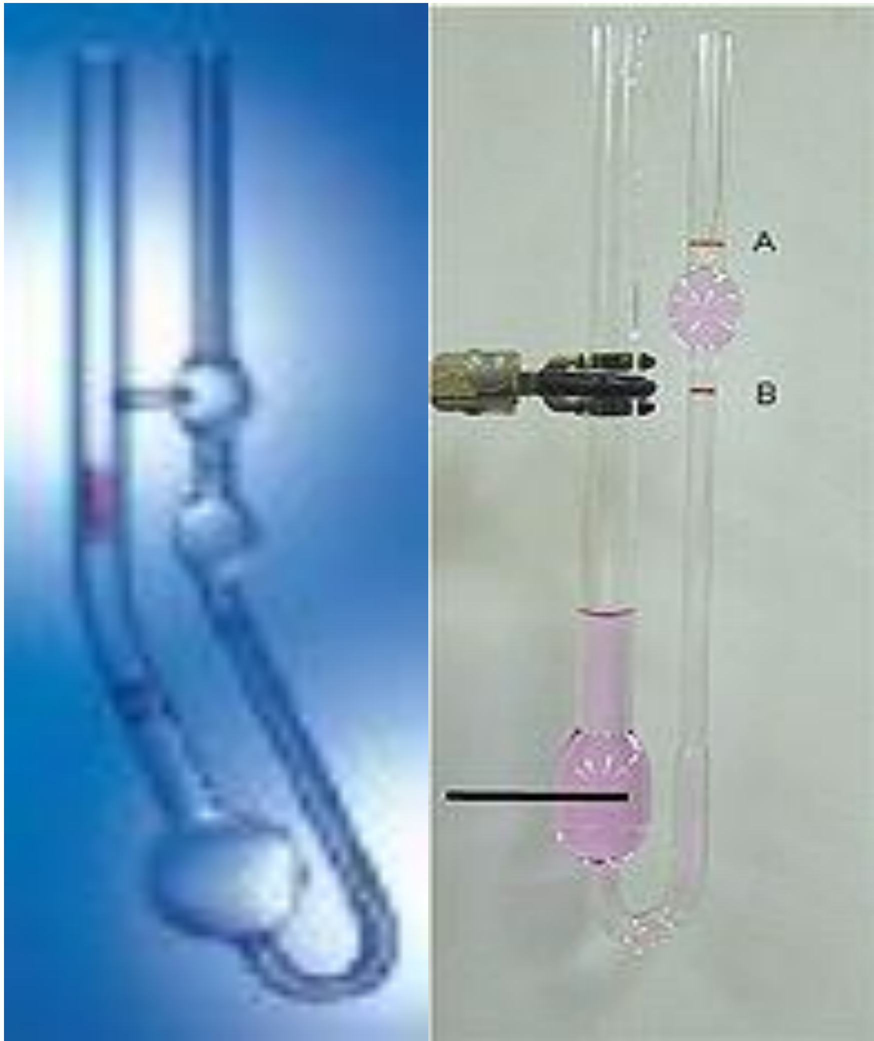
- The rate of shear in a Newtonian system is directly proportional to the shearing stress, thus one can use instruments that operate at a single rate of shear.

- For non-Newtonian system, the instrumentation used must be able to operate at a variety of rates of shear and so, only by the use of "multi-point" instruments it is possible to obtain the complete rheogram for these systems.

- So, the choice of viscometer to determine the viscosity is important, all viscometers can be used to determine the viscosity of Newtonian systems, while non- Newtonian systems need viscometer with variable shear stress.

1- Capillary Viscometer:

➢ Used for Newtonian system by determine the time required for the liquid to pass between two marks as it flows by gravity through a vertical Capillary tube known as Ostwald Viscometer



$$\eta_1 / \eta_2 = t_1 / t_2$$

Where η 1 / η 2 is called the relative viscosity

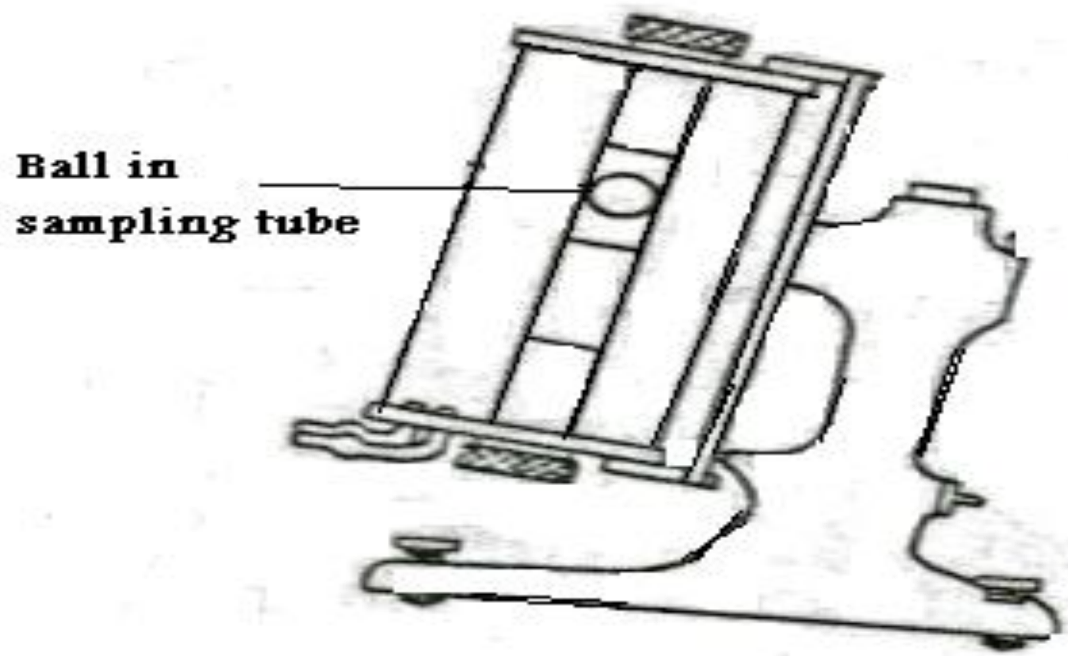
2-Falling Sphere Viscometer

- Stokes' law is the basis of the falling sphere viscometer,

$$V = 2r^2 g (\rho - \rho_o) / 9 \eta_o$$

V is the velocity of sedimentation of spherical particles, ρ is the density of the spherical particles, ρ^o is the density of the medium, η^o is the viscosity of the medium and g is the acceleration due to gravity.

For description, the fluid is stationary in a vertical glass tube and a sphere of known size and density is allowed to descend through the liquid. The time for the ball to fall between two marks is accurately measured and repeated several times .



Hoeppler Falling Ball Viscometer

$$\eta = t(S_b - S_f)B$$

where:

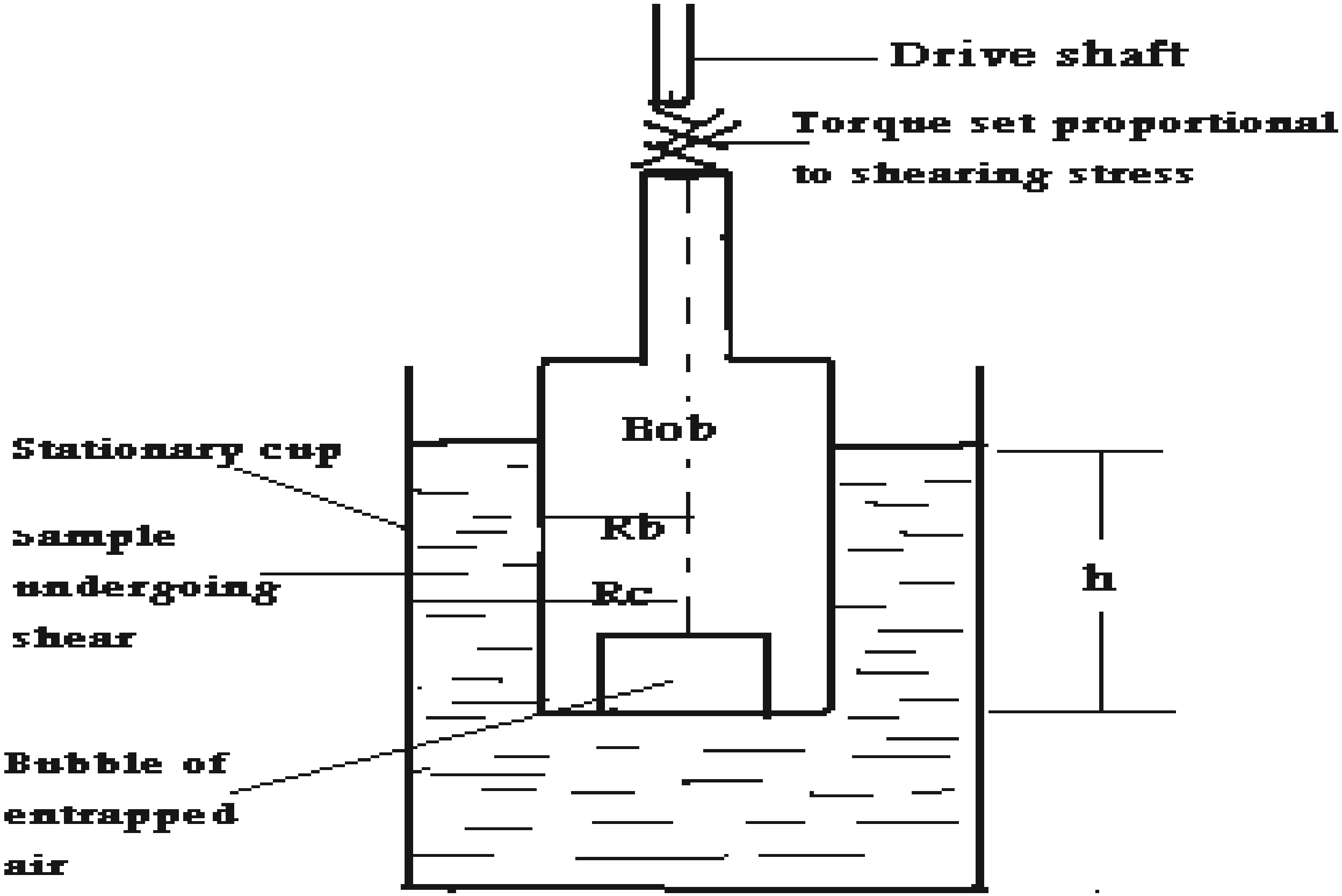
- t is the time in second for the ball to fall between two marks
- Sb , Sf are the specific gravity of the ball and the liquid
- B constant for particular ball

N.B: **Specific gravity** is the ratio of the density (mass of a unit volume) of a substance to the density (mass of the same unit volume) of a reference substance

3- Cup And Bob Viscometer:

- In the cup and Bob viscometer the sample is sheared in the space between the outer wall of the bob and the inner wall of the cup into which the bob fits.

- The various instruments available differ mainly in whether the torque set up in the bob results from the cup or from the bob being caused to resolve.



Principle of rotational cup and bob viscometer

The torque resulting from the viscous drag of the system under examination is generally measured by a spring or sensor in the drive to the bob.
Stormer instrument should be used with systems having a viscosity below 20 cps.

- $$\Omega = \frac{1}{\eta} \frac{T}{4\pi h} \left(1/R^2_b - 1/R^2_c\right)$$

Ω = (omega) T = torque in dyne cm

h= depth to which the bob is immersed in the liquid

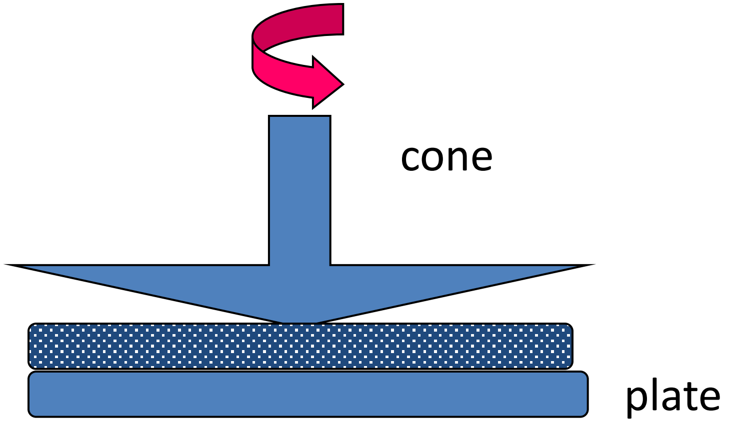
R^2_b R^2_c are the radii of the cup and bob

4- Cone and Plate Viscometer

The sample is placed at the center of the plate, which is then raised into position under the cone.

The cone is driven by a variable speed motor and the sample is sheared in the narrow gap between stationary plate and rotating cone.

The rate of shear is controlled by a selector dial and the torque (shearing stress) produced on the cone is read on indicator scale



Thank You