Rheology

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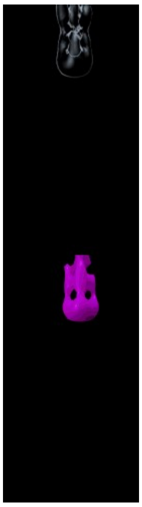
Chapter objectives

At the conclusion of this chapter student should be able to:

1. Define rheology, and describe its application in the pharmaceutical sciences and practice of pharmacy.
2. Understand and define the following concepts: shear rate, shear stress, viscosity, kinematic viscosity, fluidity, plasticity, yield point, pseudoplasticity, shear thinning, dilatancy, shear thickening, thixotropy.
3. Define and understand Newton's law of flow.
4. Differentiate flow properties and rheograms between Newtonian and non-Newtonian materials.
5. Appreciate the fundamentals of the practical determination of rheologic properties.

Rheology

Definition



- The term "rheology" (from the Greek *rheo-* "to flow " and *–logy* "science") is used to describe the flow of liquids and the deformation of solids.
- *Viscosity* is an expression for the resistance of a fluid to flow; the higher the viscosity, the greater is the resistance.
- Simple liquids can be described in terms of absolute viscosity (single value).
- Heterogeneous dispersions are more complex and cannot be expressed by a single value.

Rheology

Pharmaceutical Applications

Rheology is important in:

- Mixing and flow of materials, their packaging into containers, and their removal prior to use (pouring from a bottle, extrusion from a tube, or passage through a syringe needle).
- Selection of processing equipment used in the manufacture of pharmaceutical systems.
- Influencing patient acceptability to a particular product, physical stability, and even biologic availability.

Types of flow

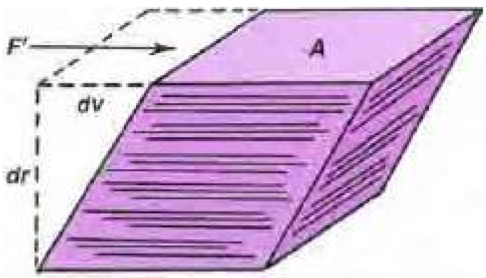
Materials are classified according to the type of flow and deformation, into two categories:

1. Newtonian systems.
2. Non-Newtonian systems.

Newtonian Systems

Newton's Law of Flow

- Consider a block of liquid consisting of parallel plates of molecules, in which the bottom layer is fixed and the top plane of liquid is moved at a constant velocity.
- The difference in velocity *(dv)* between two planes of liquid separated by the distance *(dr)* is the ***rate of shear*** *(dv/dr)* and is given the symbol *G*.
- The force per unit area *(F/A)* required to bring about flow is called the ***shearing stress*** and is given the symbol *F*.



Newtonian Systems

Newton's Law of Flow

- Shearing stress is directly proportional to rate of shear:

$$F \; \alpha \; G \quad \rightarrow F = \eta \times G$$

where η is the ***viscosity.***

- The higher the viscosity of a liquid, the greater is the shearing stress required to produce a certain rate of shear.
- Materials that obey Newton's law of flow are known as ***Newtonian systems***

Newtonian Systems

Viscosity Units

- The CGS unit of viscosity is the *poise (p)* which is defined as the shearing force required to produce a velocity of 1 cm/s between two parallel planes of liquid each 1 cm^2 in area and separated by a distance of 1 cm.
- *Centipoise (cp)* is equal to 0.01 poise and is more conveniently used for most work.
- The CGS units for poise are:

$$\text{dyne s cm}^{-2} = \text{g cm}^{-1} \text{ s}^{-1}$$

- The SI unit for viscosity is the Pa.s (1 mPa.s = 1 centipoise).

Newtonian Systems

Newton's Law of Flow

TABLE 10-1 The Viscosity of Some Newtonian Fluids at 20°C (68.0°F) at 1 atm

Fluid	Viscosity, cps
Acetone	0.34
Water	1.00
Ethanol	1.20
Olive oil	100
Glycerin, 95% (w/w)	545
Castor oil	1000

Source: Adapted from **Martin A, Bustamante P:** *Physical Pharmacy: Physical Chemical Principles in the Pharmaceutical Sciences*, 4th ed. Philadelphia: Lea & Febiger, 1993.

Newtonian Systems

Fluidity

- ***Fluidity (ϕ)*** is defined as the reciprocal of viscosity:

$$\phi = 1/\eta$$

Newtonian Systems
Kinematic Viscosity

- ***Kinematic viscosity*** is the absolute viscosity (η) divided by the density of the liquid (ρ) at a specific temperature:

$$v = \frac{\eta}{\rho}$$

- The SI units will be $m^2\ s^{-1}$
- The cgs units of kinematic viscosity are the *stoke (S)* and the *centistoke (cS).*
- *1 S* = $cm^2\ s^{-1}$

Newtonian Systems
Relative Viscosity

- The viscosity ratio or relative viscosity (η_r) of a solution is the ratio of the solution viscosity to the viscosity of the solvent (η_0):

$$\eta_r = \frac{\eta}{\eta_o}$$

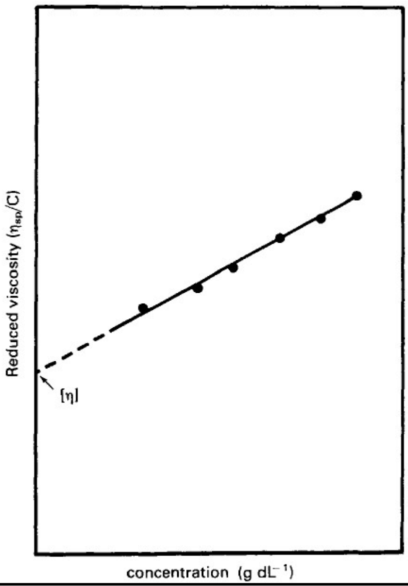
- The specific viscosity (η_{sp}) is given by:

$$\eta_{sp} = \eta_r - 1$$

Newtonian Systems

Intrinsic Viscosity

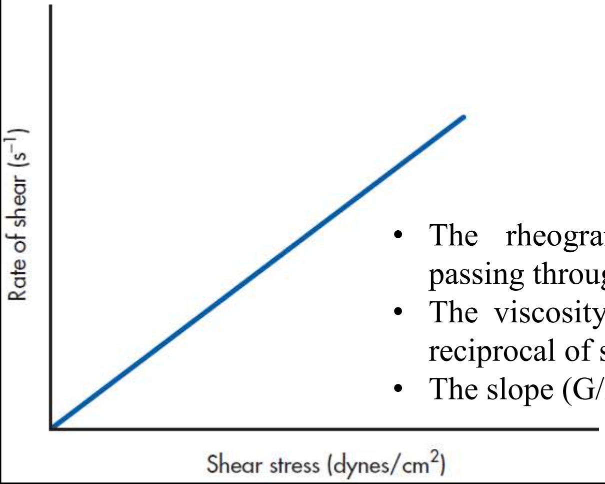
- If η_{sp}/C *is* determined at a range of polymer concentrations and plotted as a function of concentration, then a linear relationship should be obtained.
- The intercept produced on extrapolation of the line to the ordinate will yield the constant which is referred to as the limiting viscosity number or the intrinsic viscosity,$[\eta]$, when the units of concentration are in g dL^{-1}.



Newtonian Systems

Rheogram

- A representative flow curve (rheogram) for a Newtonian system.



- The rheogram is a straight line passing through the origin.
- The viscosity is constant and is the reciprocal of slope.
- The slope (G/F) is termed **fluidity**.

Newtonian Systems

Effect of temperature on viscosity

- The viscosity of Newtonian fluids *decreases* sharply with increasing temperature.
- The temperature dependence of viscosity is expressed by the following equation, which is analogous to the Arrhenius equation:

$$\eta = A \exp^{Ev/RT}$$

- The linearized logarithmic form of the equation is:

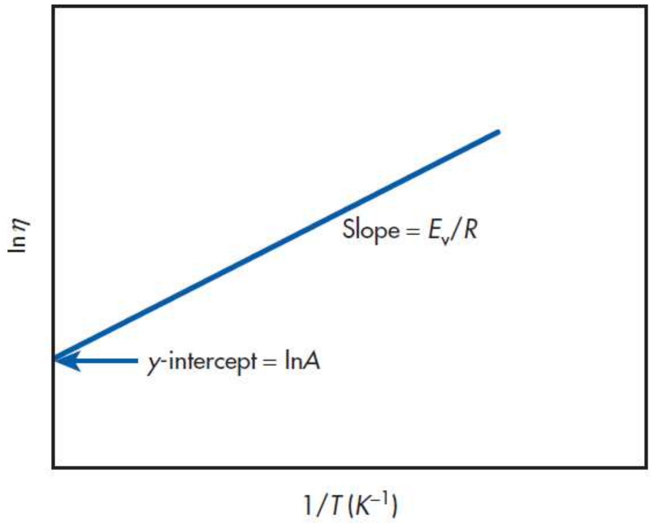
$$\ln \eta = \ln A + Ev/R(1/T)$$

- Where: *A* is a constant (has the same units as viscosity),
- *Ev* is known as the activation energy required to initiate the flow of molecules, and *R* is the universal gas constant.

Newtonian Systems

Effect of temperature on viscosity

- The graph of $\ln \eta$ versus $1/T$ is linear with a slope = Ev/R



Newtonian Systems

Effect of temperature on viscosity

Example: The viscosity of human plasma at 37°C is 1.2 cps. Assuming that plasma behaves as a Newtonian fluid, determine the viscosity of plasma required for an infusion that is kept at room temperature (25°C). The activation energy of plasma is 4.25×10^3 cal/mole.

Solution:

- First, using the equation $\ln \eta = \ln A + Ev / R(1/T)$,
- determine the A value by using the parameters at 37°C ($T = 310$ K):
- $\ln(1.2) = \ln A + [(4.25 \times 10^3/1.987)][(1/310)]$
- $0.182 = \ln A + 6.90 \rightarrow \ln A = -6.718 \rightarrow A = 1.21 \times 10^{-3}$ cps
- Using the A value, calculate the viscosity at 25°C (or $T = 298$ K):
- $\ln \eta_{25} = \ln(1.21 \times 10^{-3}) + [(4.25 \times 10^3/1.987)][(1/298)]$
- $\eta_{25} == 1.58$ cps

Non-Newtonian Systems

- The majority of fluid pharmaceutical products are not simple liquids and do not follow Newton's law of flow.
- These systems are referred to as ***non-Newtonian.***
- Non-Newtonian behavior is generally exhibited by liquid and solid heterogeneous dispersions (e.g. colloids, emulsions, suspensions, and ointments).
- According to the rheograms of non-Newtonian materials, three classes of flow are recognized:

1. Plastic Flow (or ***Bingham Flow)***

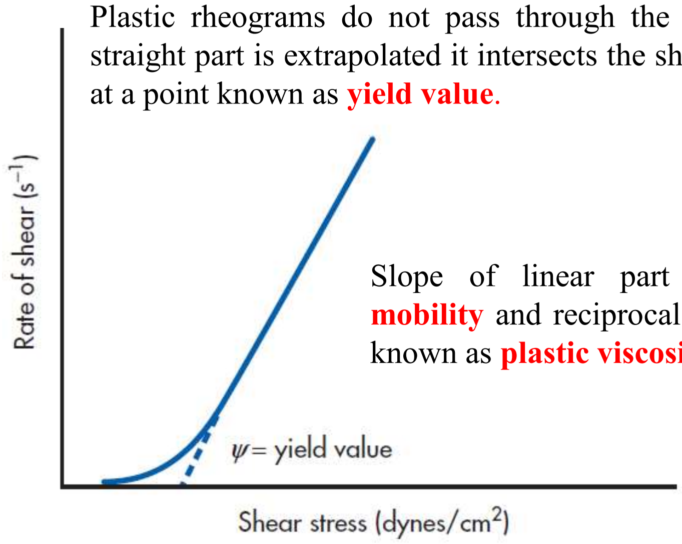
2 ***Pseudoplastic Flow***

3. ***Dilatant Flow***

Non-Newtonian Systems

Plastic flow (Bingham Flow)

Plastic rheograms do not pass through the origin but when straight part is extrapolated it intersects the shearing stress axis at a point known as **yield value**.



Slope of linear part is termed **mobility** and reciprocal of slope is known as **plastic viscosity**.

Non-Newtonian Systems

Plastic flow

- The equation describing plastic flow is

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

f = Yield value (dyne/cm^2)

- A plastic (Bingham) body does not begin to flow until a shearing stress exceeds the yield value.
- At stresses below the yield value, the substance acts as an elastic material.

Non-Newtonian Systems

Plastic flow

- Plastic flow is associated with the presence of flocculated particles in concentrated suspensions.
- A yield value exists because of the contacts between adjacent particles (via van der Waals forces), which must be broken before flow can occur.
- The more flocculated the suspension, the higher will be the yield value.

Non-Newtonian Systems

Plastic flow

Example: Calculating Plastic Viscosity

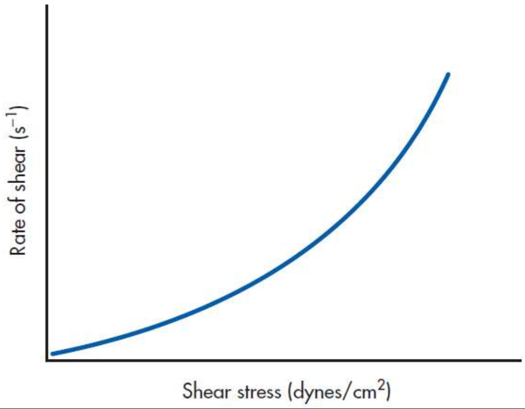
A plastic material was found to have a yield value of 5200 dynes/cm2. At shearing stresses above the yield value, *F* was found to increase linearly with *G*. If the rate of shear was 150 sec^{-1} when *F* was 8000 dynes/cm^2, calculate *U*, the plastic viscosity of the sample.

U = (8000-5200)/150 = 18.67 poise

Non-Newtonian Systems

Pseudoplastic flow (Shear thining systems)

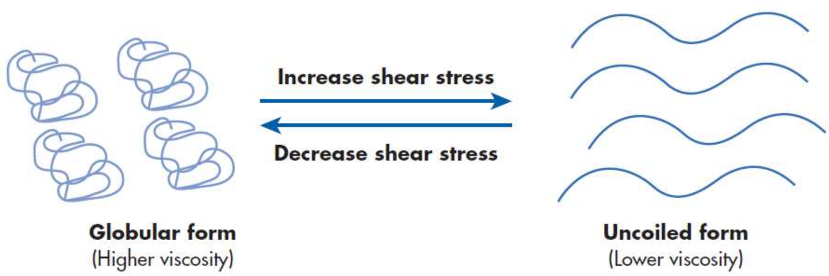
- No part of curve is linear ⇒ Viscosity is decreasing with shear stress.
- An apparent viscosity can be obtained at any shear rate from the slope of tangent to the curve at the specified point.



Non-Newtonian Systems

Pseudoplastic flow (Shear thining systems)

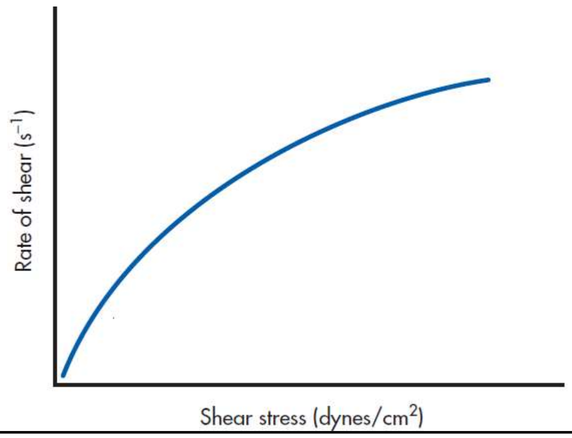
- The pseudoplastic flow is associated with the presence of materials with long-chain molecules (e.g. linear polymers).
- As shearing stress is increased, normally disarranged molecules begin to align in the direction of flow, reducing internal resistance of the material, and allowing a greater rate of shear.



Non-Newtonian Systems

Dilatant Flow (Shear-Thickening Systems)

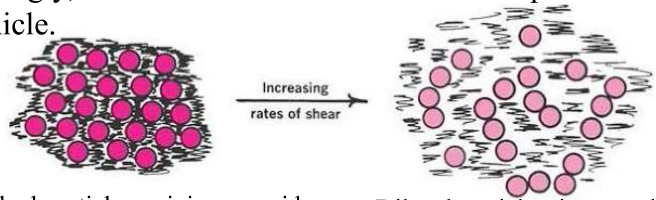
- Materials with dilatant flow exhibit an increase in viscosity with increasing shearing rate (reverse to pseudoplastic system).



Non-Newtonian Systems

Dilatant Flow (Shear-Thickening Systems)

- Dilatant rheology is observed with suspensions that contain a very high (> 40% to 50%—w/w) solid content.
- At low rates of shear, particles are closely packed with minimal voids, allowing the vehicle to fill the voids and permits particles to move relative to one another
- As shear stress is increased, the system dilates; making the vehicle insufficient to fill the increased voids between particles.
- Accordingly, resistance to flow increases due to poor lubrication by the vehicle.



Close-packed particles; minimum voids; sufficient vehicle; low consistency

Dilated particles; increased void volume; insufficient vehicle; high consistency

Non-Newtonian Systems

Power law equation

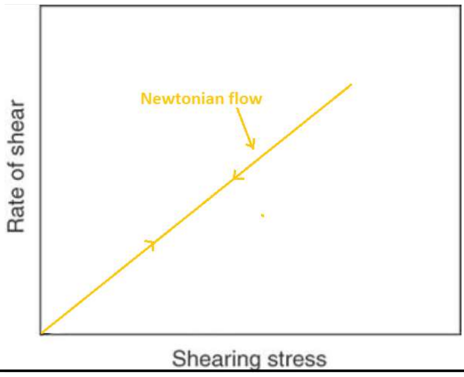
- The pseudo plastic and dilatant flow can be described using the following equation:

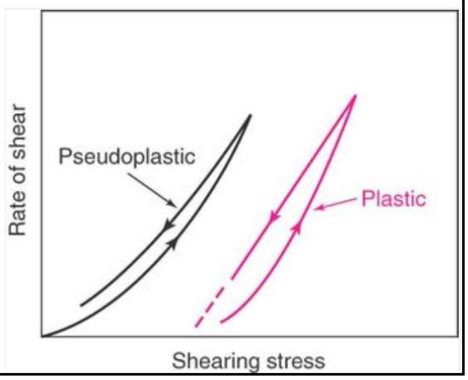
$$\eta' = \frac{F^n}{G}$$

n < 1	**Pseudoplastic**
n = 1	**Newtonian**
n > 1	**Dilatant**

Thixotropy

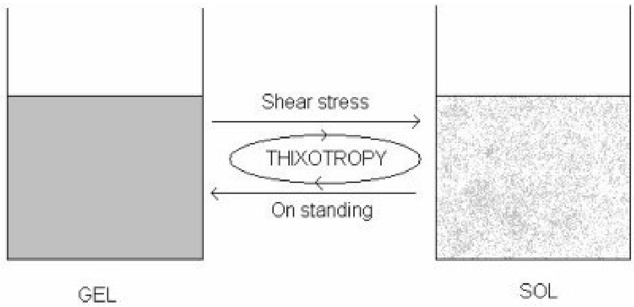
- In Newtonian systems if the rate of shear was reduced once the desired maximum had been reached, the downcurve would be identical with, and superimposable on, the upcurve.
- With shear-thinning systems (i.e., pseudoplastic), the downcurve is frequently displaced to the left of the upcurve.





Thixotropy

- The lower consistency of a material on the downcurve indicates a breakdown of structure that does not reform immediately when stress is removed.
- This is known as ***thixotropy,*** which can be defined as "relatively slow recovery (on standing) of a material consistency, lost through shearing."



Applications of thixotropy

Creams and Ointments

- Formulation should spread easily on the skin and retain its original form on removal of stress in order to adhere at the site of application

Injections (e.g. Procaine Penicillin)

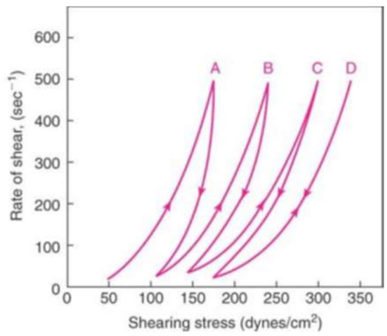
- Transform from gel to sol when passing through hypodermic needle then revert to gel at the site of intramuscular injection where the drug is slowly released in the body

Suspensions

- The suspension exist as a gel in resting state. Upon shaking, the gel will convert into a solution, then reverts back to a gel upon storage.

Anti-thixotropy

- In this case, the systems shows a time-dependent increase in viscosity.
- The longer the fluid undergoes shearing force, the higher its viscosity.
- The downcurve is displaced to the right of the upcurve.
- E.g. magnesia magma



Rheogram of magnesia magma

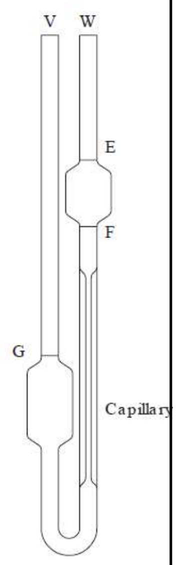
Determination of Rheological Properties

- Because shear rate in a Newtonian system is directly proportional to shearing stress (the rheogram is a straight line), a complete rheogram can be obtained form a single point determination. Therefore instruments that operate at a single shear rate can be used.
- In non-Newtonian systems, multiple point determination is required to obtain a complete rheogram (a single-point determination is useless). Therefore, instruments that can operate at a variety of shear rates are used.

Determination of Rheological Properties
Newtonian fluids

Capillary viscometer (e.g. U-tube viscometer)

- Liquid is introduced through arm V up to mark G using a pipette.
- The viscometer is then clamped vertically in a constant-temperature water bath and allowed to reach the required temperature.
- The level of the liquid is adjusted and is then blown or sucked into tube W until the meniscus is just above mark E.
- The time for the meniscus to fall between marks E and F is then recorded.
- Determinations should be repeated until three readings all within 0.5 seconds are obtained.



A U-tube viscometer.

Determination of Rheological Properties
Newtonian fluids

Capillary viscometer (e.g. U-tube viscometer)

- when the flow times or two liquids are compared using the same viscometer:

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \quad \text{or} \quad \frac{v_1}{v_2} = \frac{t_1}{t_2}$$

- For a given viscometer a standard fluid such as water can be used or the purposes of calibration and equation becomes:

$$v = ct$$

Determination of Rheological Properties
Newtonian fluids

Capillary viscometer (e.g. U-tube viscometer)

Example Viscosity of Acetone

- The time required for acetone to flow between the two marks on the capillary viscometer was 45sec and for water the time was 100 sec, at 25°C. The density of acetone is 0.786 g/cm3 and that of water is 0.997 g/cm3 at 25°C. The viscosity of water is 0.8904 cp at this temperature.
- The viscosity of acetone at 25°C can be calculated using equation

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \Rightarrow \quad \frac{\eta_1}{0.8904} = \frac{0.786 \times 0.45}{0.997 \times 100} \Rightarrow \quad \eta_1 = 0.316 \text{ cp}$$

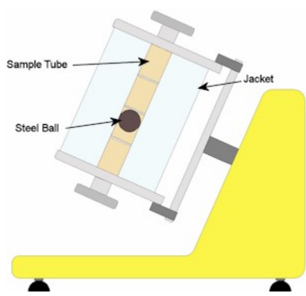
Determination of Rheological Properties
Newtonian fluids

Falling-sphere viscometer

- This viscometer is based upon Stokes' Law. When a body falls through a viscous medium, it experiences a resistance or viscous drag which opposes the downward motion:

$$\eta = \frac{d^2 g(\rho_s - \rho_l)}{18u}$$

$$v = \frac{d^2 g(\rho_s - \rho_l)}{18u\rho_l}$$



Determination of Rheological Properties
non-Newtonian fluids

Rotational viscometers

Cup and pop viscometer

Cone and plate viscometer