Physical Pharmacy II

2nd stage

College of Pharmacy

Lec: 4

Rheology

By : Dr. Nizar Awish Jassem

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- **Rheology:** The word *rheology* comes from the Greek word **"rheo"** meaning *to flow* and **"logos"** meaning *science*.
  - So, **rheology is the science that studies:**
    - The **flow of liquids**
    - The **deformation of solids**
  - In pharmacy, this is extremely important because many dosage forms are not simple liquids.
    - For example :Creams, Ointments, Pastes, Lotions, Suspensions, and Emulsions , All of these must flow properly during:
      - Manufacturing
      - Filling into containers
      - Application by the patient
  - One of the most important concepts in rheology is **viscosity**.
  - **Viscosity is the resistance of a fluid to flow.**
    - High viscosity → thick fluid (like honey)
    - Low viscosity → thin fluid (like water)
  - For **simple liquids**, viscosity can be described using a single value called **absolute viscosity**.
  - However, for **heterogeneous dispersions** (like emulsions and suspensions), flow behavior is more complex and cannot be described by a single constant value.

Important of Rheology in Pharmacy

- Rheology affects:
  - **Manufacturers** of **medicinal and cosmetic creams, pastes, and lotions** must be capable of producing products with acceptable consistency and smoothness. A cream that is too thick cannot be spread easily.
  - Valuable information can be obtained by use of analytic methods of rheology, for formulating better pharmaceutical products.
  - **The rheology** of product can affect patient acceptability, physical stability, and even biologic availability.
  - Rheologic properties of a pharmaceutical system can influence the selection of processing equipment. **For example** :A product that is too viscous may be difficult to pump during manufacturing.

Classes of materials according to types of flow:

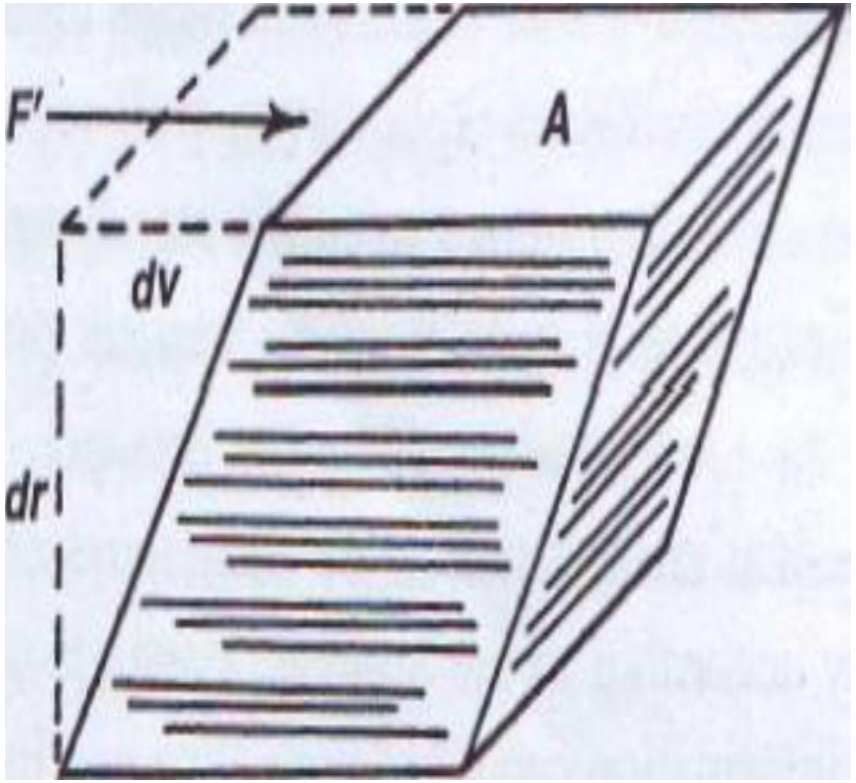
1. Newtonian systems
2. Non-Newtonian systems.

Newtonian Systems.

- **Newton's Law of Flow**
  - Newton discovered that for certain liquids:
    - ❑ **The rate of shear is directly proportional to the shearing stress**.
  - **Shearing Stress :**The force applied per unit area to make a liquid flow.
- Mathematically:

$$\text{Shearing stress} : \left(\frac{F'}{A}\right) = F$$

where: F⁻ = force applied, A = area



Rate of Shear (dv/dr)

- The rate of shear represents *How fast one layer of liquid moves relative to another*.
- It is written as:

Rate of shear or the velocity gradient: **(dv/dr) =G**

where:

dv = difference in velocity between two layers

dr = distance between those layers

- Newton was recognized that the higher the viscosity of a liquid, the greater is the force per unit area (shearing stress) required to produce a certain rate of shear.
- Hence, **rate of shear should be directly proportional to shearing stress**, or

$$\frac{F'}{A} = \eta \frac{dv}{dr}$$

Where, **η** is the coefficient of viscosity, usually referred to simply as **viscosity**

- Above equation is frequently written as

$$\eta = \frac{F}{G}$$

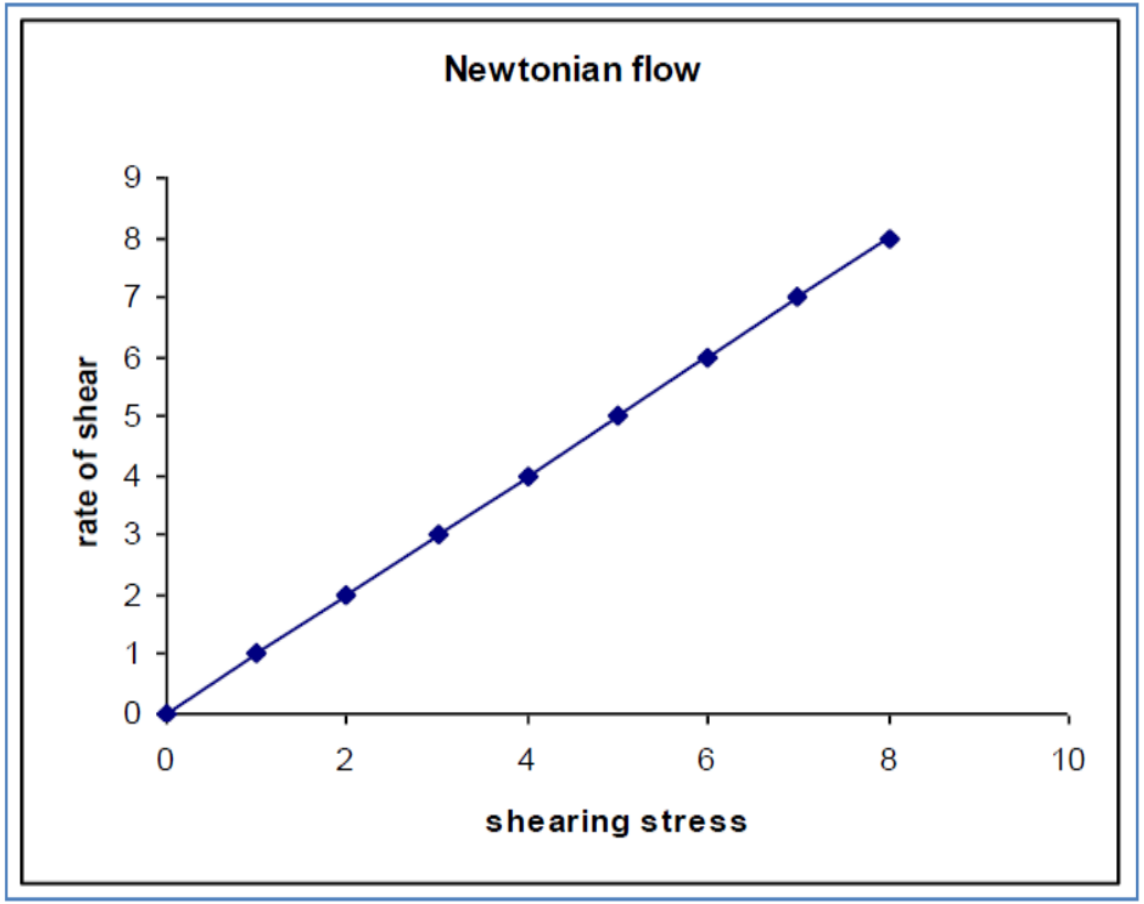
where, F = F'/A and G = dv/dr.

F = shearing stress

G = rate of shear

Flow Curve (Rheogram)

- If we plot:
  - Shearing stress (x-axis)
  - Rate of shear (y-axis)
- **For a Newtonian liquid**, we get:
  - ➢ A straight line passing through the origin.
  - This means:
    - If you double the force, the rate of flow doubles.
    - **Viscosity** remains **constant**.
      - It does not change with applied stress.
- **Examples of Newtonian Liquids:** Water, Alcohol, Glycerine and Light oils



Units of Viscosity

- The classical **unit** of viscosity is **Poise (P) ;** Defined as the shearing force required to produce a velocity of 1 cm/sec between two layers of liquid 1 cm apart.
    - The units for **poise** are **dyne sec cm^{-2}** or **g cm^{-1} sec^{-1}**
  - More commonly used unit:
    - **Centipoise (cP) :** 1 cp being equal to 0.01 poise.
    - ✓ Water ≈ 1 cP at room temperature

- **Fluidity** (ϕ) is simply It is the **reciprocal** of **viscosity**.

$$\varphi = \frac{1}{\eta}$$

Kinematic Viscosity

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

$$\text{Kinematic viscosity} = \frac{\eta}{\rho}$$

The units of kinematic viscosity are the **stoke** (s) and the **centistoke** (cs).

Why Divide by Density?

- Two liquids may have:
  - The same resistance to flow (same **η**)
  - But different densities
  - ➢ Density affects how the liquid behaves under gravity. So, kinematic viscosity tells us: How fast a liquid flows under its own weight.

Note:

- Water is ordinarily used as a standard for viscosity of liquids.
- Its viscosity at 25°C is 0.8904 cp.

- Absolute viscosities of some Newtonian liquids at 20 C° commonly used in pharmacy are given in this table

Liquid	Viscosity (cp)
Castor oil	1000
Olive oil	100
Water	1.0019

Temperature Dependence and the Theory of Viscosity

❑ Temperature Dependence of Viscosity

- When temperature increases:
  - Viscosity **decreases**
  - Fluidity of a liquid (the reciprocal of viscosity) (1/η) **increases**

Theoretical Explanation

- The dependence of the viscosity of a liquid on temperature is expressed approximately for many substances by an equation analogous to the Arrhenius equation of chemical kinetics:

$$\eta = A\exp\left(\frac{E_a}{RT}\right)$$

where **A** is a constant depending on the molecular weight and molar volume of the liquid and **Ea**, is an "activation energy" required to initiate flow between molecules. **R** is the gas constant, and **T** = absolute temperature (Kelvin)

Non-Newtonian Systems

- Most of the liquid pharmaceutical products encounter by liquid and solid heterogeneous dispersions such as — such as **emulsions, suspensions, colloidal solutions, and ointments** — do **not** behave like simple liquids such as water.
- These systems do not follow **Newton's law of flow**, so we call them **non-Newtonian fluids**.
- When we study these materials using a **rotational viscometer**, and results are plotted, various consistency curves, we obtain different types of flow curves (called rheograms).
- From these curves, we classify non-Newtonian flow into three main types:

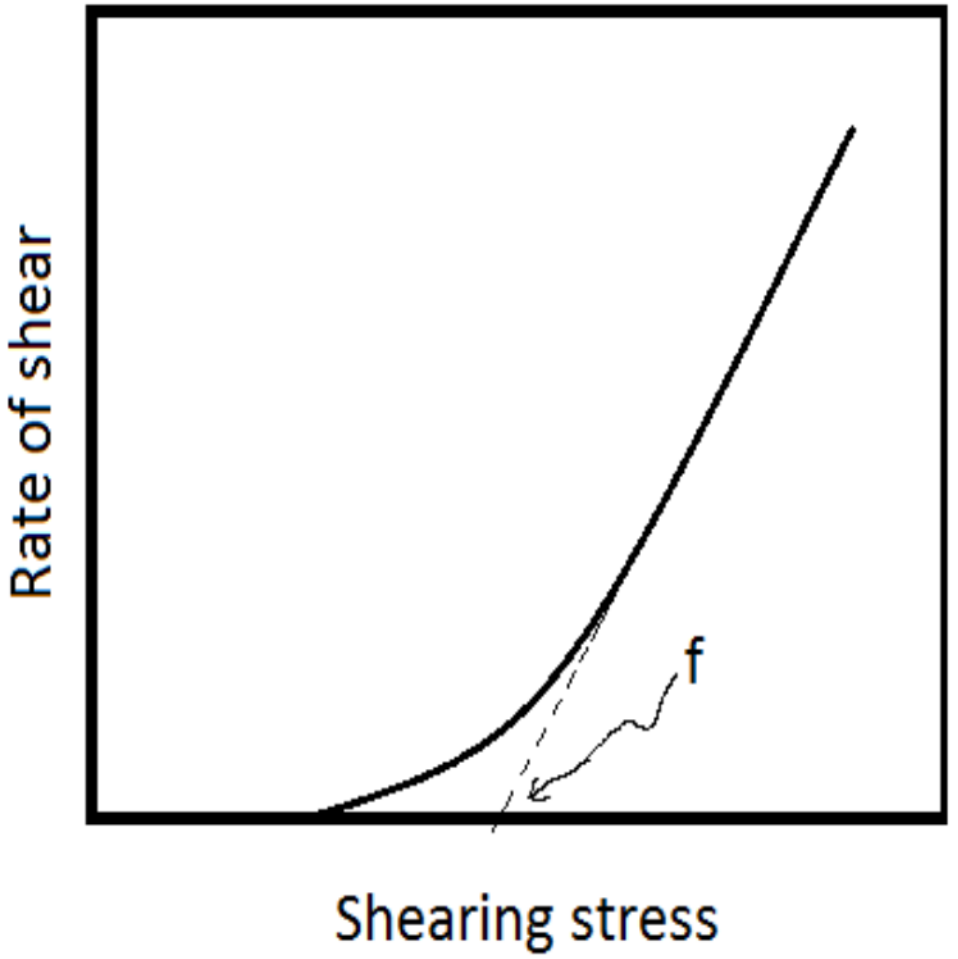
  1.Plastic flow

  2.Pseudoplastic flow

  3.Dilatant flow

Plastic Flow (Bingham Bodies)

- Plastic flow materials are also known as **Bingham bodies**.
- **Yield Value**
- Unlike Newtonian fluids, plastic materials:
  - **Do not start flowing immediately** when stress is applied.
  - They require a **minimum force**, called the **yield value**, before flow begins.
    - Below the yield value : The material behaves like an **elastic solid**.
    - Above the yield value: The material begins to flow like a liquid.
- In the rheogram (graph of shear stress vs. rate of shear):
  - The curve does **not pass through the origin**.
  - It intersects the shear stress axis at the **yield value**.
    - This yield value is extremely important in pharmaceutical suspensions.



Plastic Viscosity

- After the yield value is exceeded:
  - The slope of the straight line in the rheogram represents the **mobility**. analogous to fluidity in Newtonian systems
  - The reciprocal of mobility is called the **plastic viscosity (U)**.

The equation describing plastic flow is:

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

Where:
F = applied shear stress
f = yield value
G = rate of shear

Practical Example : toothpaste

- It does not flow out of the tube on its own.
- You must squeeze the tube (apply stress).
- Once sufficient force is applied, it flows.

➢ That is **plastic flow behavior**

- **Plastic flow** is common in **concentrated suspensions** that contain **flocculated particles**.
  - In these systems:
    - Particles form a network structure.
    - The particles are held together by weak forces (like van der Waals forces).
    - This structure must be broken before flow can occur.
  - The more flocculated the suspension, the **higher the yield value**.
    - This is beneficial in pharmacy because:
      - At rest → high yield value prevents sedimentation.
      - When shaken → structure breaks → suspension flows easily for pouring.

Pseudoplastic Flow (Shear-Thinning Systems)

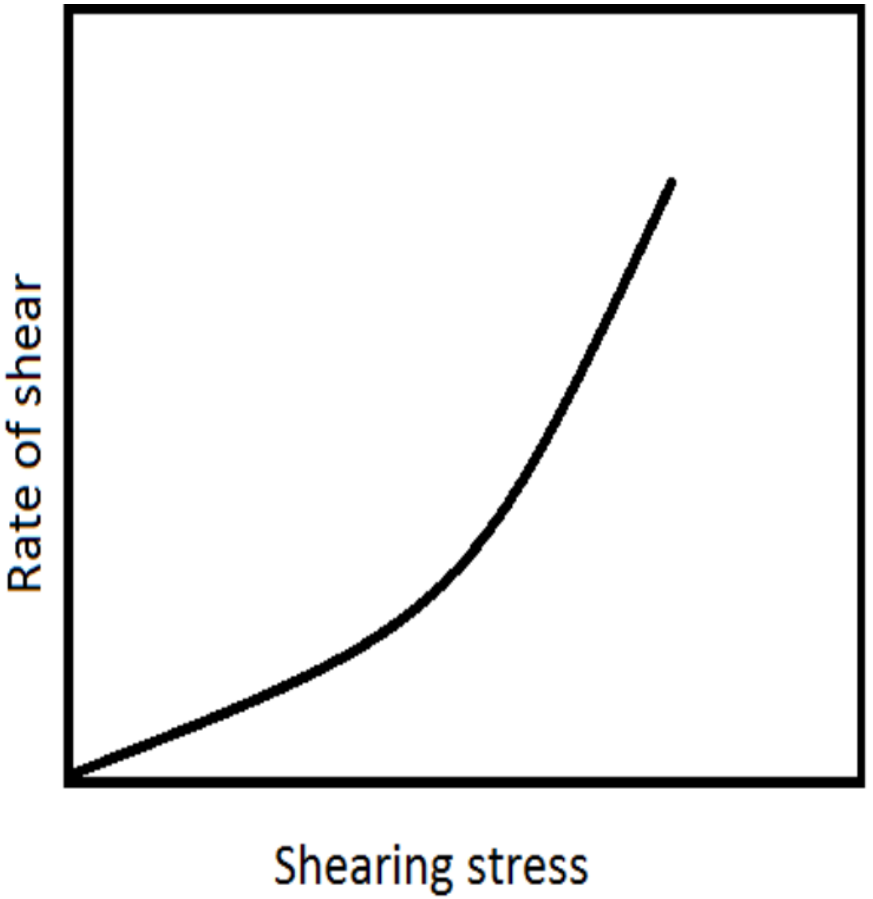
- Many pharmaceutical products, including **liquid dispersions of natural and synthetic gums** (e.g., sodium alginate, and methylcellulose) exhibit **pseudoplastic flow**.
- Pseudoplastic flow systems usually contain **long-chain polymers in solution**, not flocculated particles like plastic systems.

As seen in this Figure:

❑ **No Yield Value**

- The flow curve **starts at the origin**.
- This means the material begins to flow immediately when stress is applied.
- There is **no yield stress**.
- As we increase stirring or shaking, the viscosity **decreases**.
- This behavior is called **shear-thinning**.
- The curve on the rheogram is Curved (not straight) - Non-linear

- In polymer solutions:
  - At rest, polymer chains are randomly arranged and entangled.
  - When shear is applied, the chains align in the direction of flow.
  - This alignment reduces resistance → viscosity decreases.



Pseudoplastic Flow (Shear-Thinning Systems)

- Because the curve is not linear We cannot describe it using a single viscosity value.
- Instead, An **apparent viscosity** can be obtained at any rate of shear from the slope of the tangent to the curve at the specified point.
- Objective comparisons between different pseudoplastic systems are more difficult than with either Newtonian or plastic systems.
- For example, **Newtonian systems** are completely described by **viscosity, η**, and plastic systems are adequately described by yield value, f, and plastic viscosity, U.
- However, the **exponential formula** can be used to compare rheology of **pseudoplastic materials** to be compared.

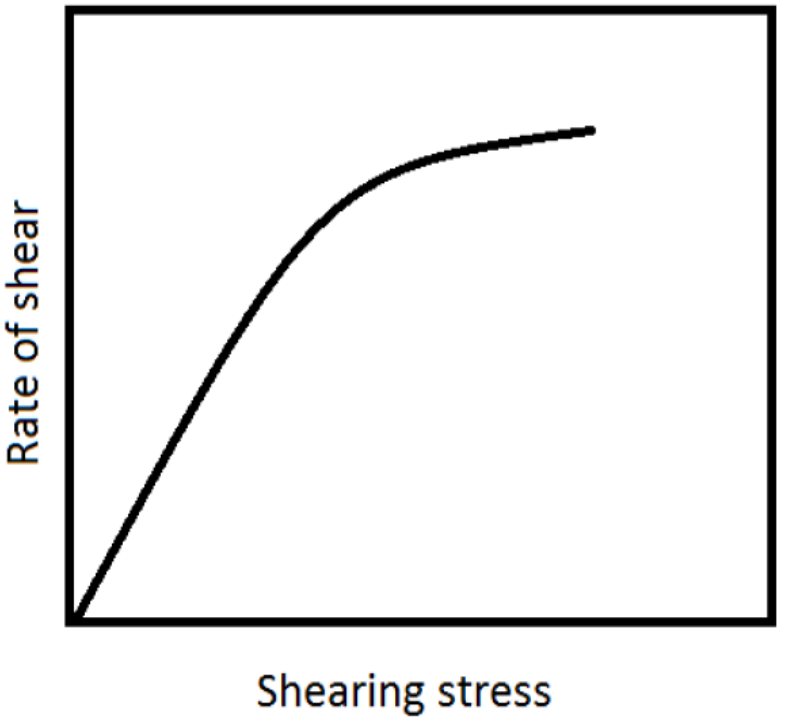
$$F^N = \eta\ 'G$$

N : flow behavior index, **η** ' is a viscosity coefficient

- The exponent **N** rises as flow becomes increasingly non-Newtonian
- When N = 1, the equation reduces to equation $(\eta = \frac{F}{G})$ and flow is **Newtonian**.
- **Practical Examples are** Ketchup and Polymer gels

Dilatant Flow (Shear-Thickening Systems)

- Dilatant systems is Increase resistance to flow when shear rate increases so called **shear-thickening systems**.
- Such systems actually increase in volume when sheared and are hence termed dilatant; Figure illustrates their flow properties.
- This type of flow is the inverse of that possessed by pseudoplastic systems.
- Whereas pseudoplastic materials are frequently referred to as "shear-thinning systems," dilatant materials are often termed "shear-thickening systems." When stress is removed, a dilatant system returns to its original state of fluidity.

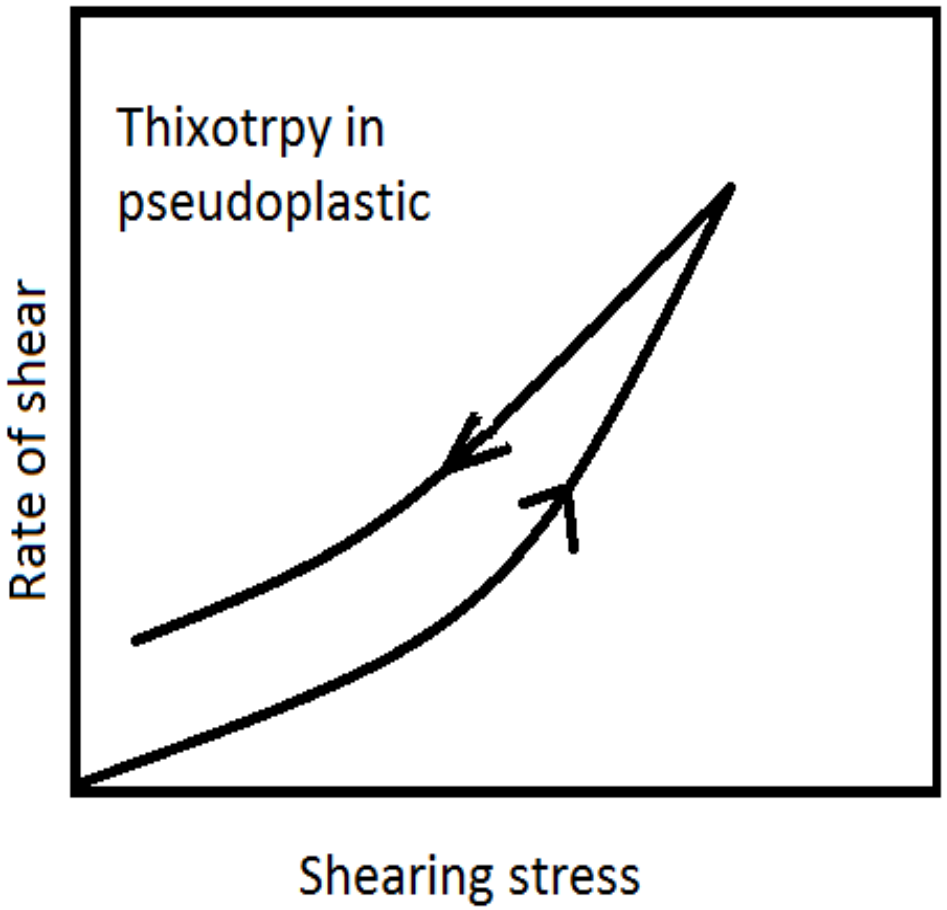


- Equation ($F^N = \eta ' G$) can be used to describe dilatancy in quantitative terms. In this case, **N is always less than 1** and decreases as degree of dilatancy increases.
- As N approaches 1, the system becomes increasingly Newtonian in behavior.
- Substances possessing dilatant flow properties are occur in Suspensions containing a **high concentration (≈ 50% or more)** of small, deflocculated particles
- Classic example: Cornstarch mixed with water. Move slowly → behaves like liquid, Hit it quickly → behaves like solid

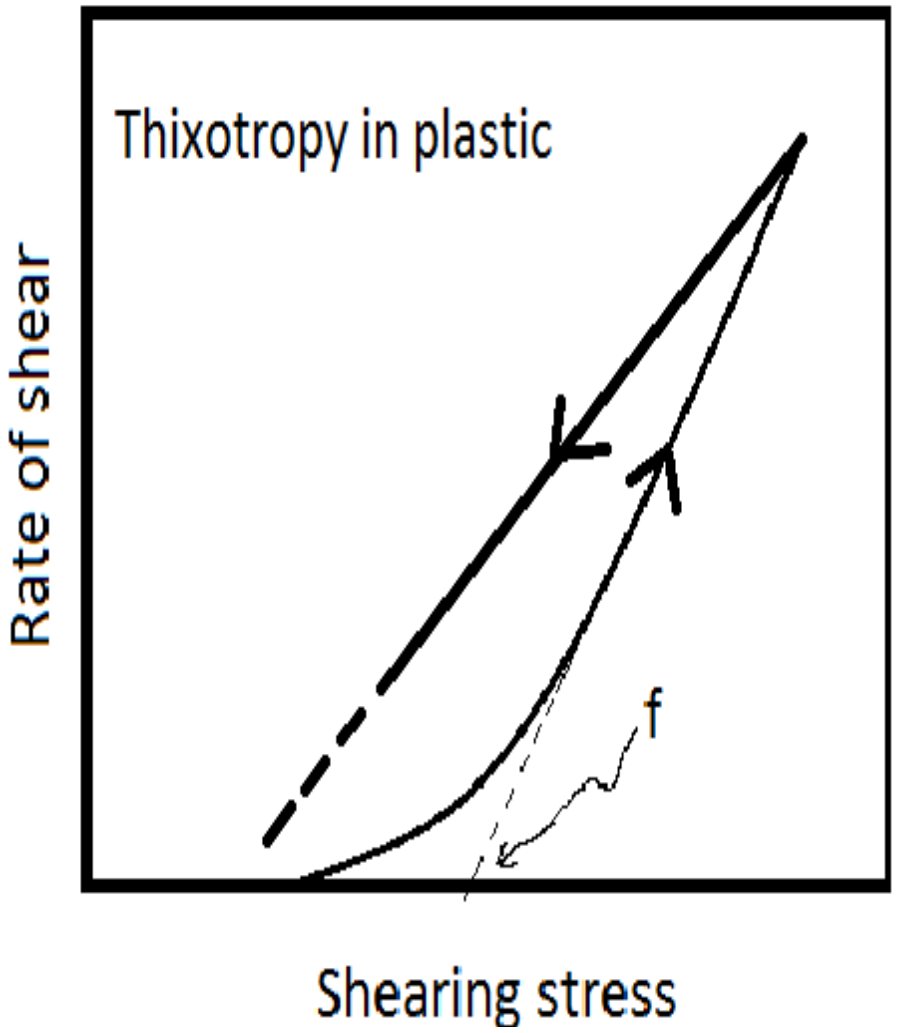
Property	Plastic	Pseudoplastic	Dilatant
Yield value	Yes	No	No
Curve starts at origin	No	Yes	Yes
Viscosity with shear	Constant after yield	Decreases	Increases
Also called	Bingham body	Shear-thinning	Shear-thickening

THIXOTROPY

- Several types of behavior are observed when rate of shear is progressively increased and plotted against resulting shear stress.
- If the rate of shear were reduced when the maximum had been reached, and the resulted downcurve is identical with the upcurve, this system is **Newtonian systems**.
- With **shear-thinning systems** (i.e., pseudoplastic), the **down curve** is frequently displaced to the **left** of the up curve (Figure), showing that the material has a lower consistency at the down curve than at up curve.
- This phenomenon, known as **thixotropy**, can be defined as "an isothermal and comparatively slow recovery, on standing of a material, of a consistency lost through shearing.“
- Typical rheograms for **plastic and pseudoplastic systems exhibiting this behaviour** are shown in the following Figure.

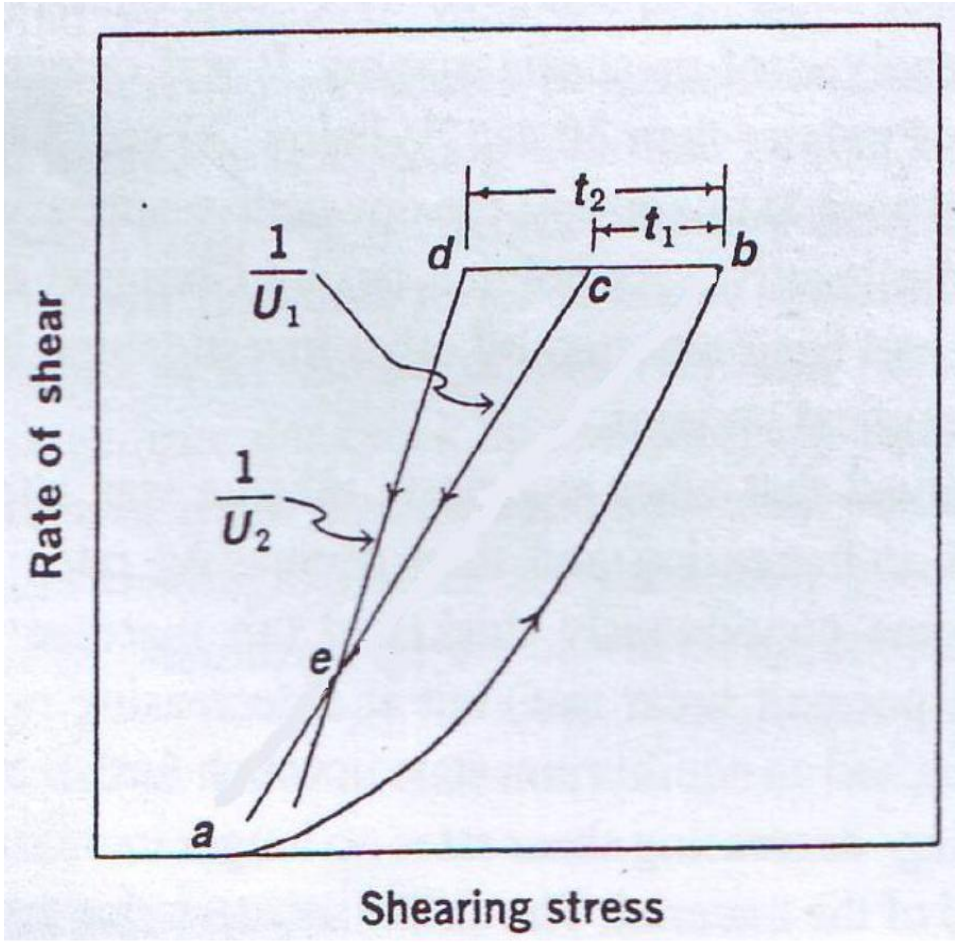


- Rheograms obtained with **thixotropic materials** are highly dependent on the rate at which shear is increased or decreased and the length of time a sample is subjected to any one rate of shear.
- For thixotropic materials:
  - When shear rate increases → material structure breaks down.
  - When shear rate decreases → structure has **not fully recovered.**
  - Therefore, the **down-curve shifts to the left** of **the up-curve.**
- **Hysteresis loop**: Is the area between the up-curve and down-curve of rheogram.
- So the **rheogram for same product** is <u>different</u> depending on *time of shear, rate of shear, and degree of structure in the sample.*
- This is an important point to bear in mind when attempting to obtain a quantitative measure of thixotropy.



Measurement of Thixotropy

- **The area of hysteresis** has been proposed as a measure of thixotropic breakdown; it can be obtained readily by means of a planimeter or other suitable technique.
- With **plastic** (Bingham) bodies, **two approaches** are frequently used to **estimate degree of thixotropy**.
- **The first** is to ***determine structural breakdown with time at a constant rate of shear***. (the maximum shear rate is constant, the time of holding before reducing shearing stress is different)
- Based on such a rheogram, a **thixotropic coefficient, B**, the rate of breakdown with time at constant shear rate, is calculated as follows:



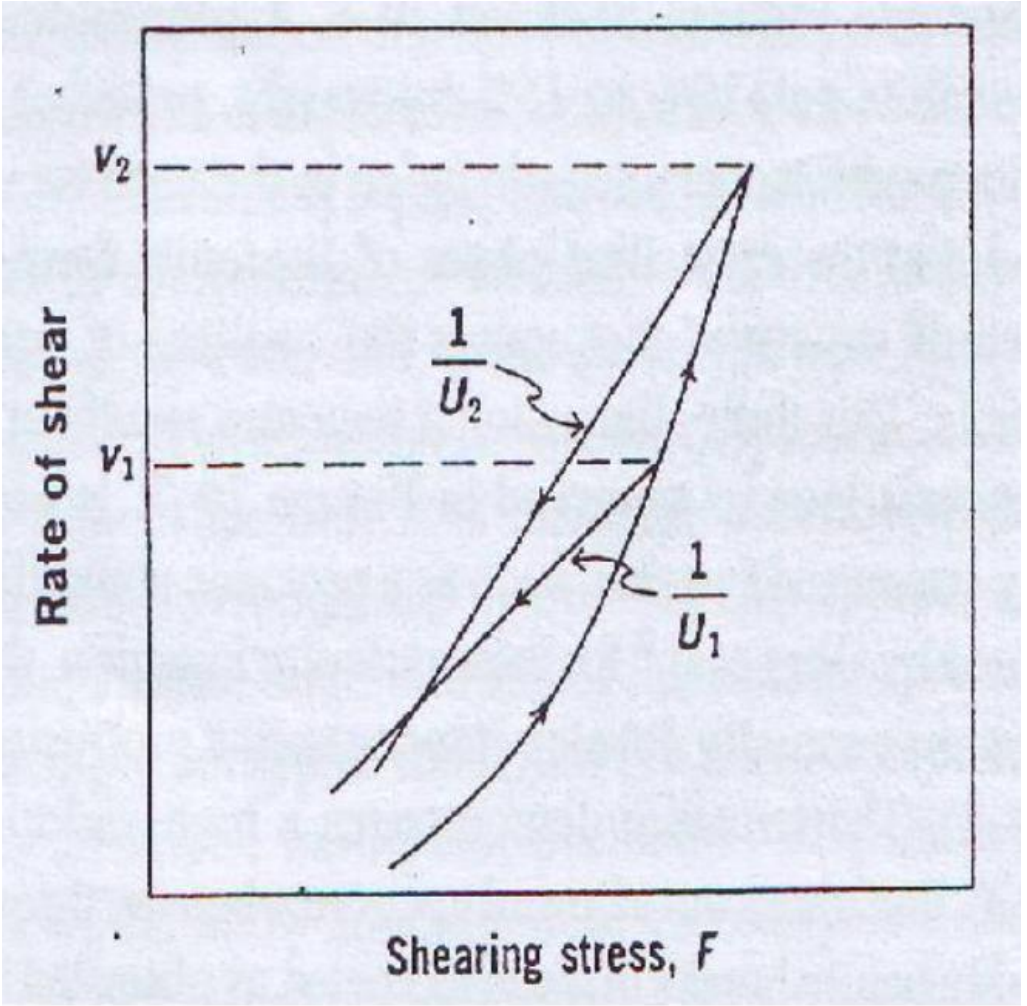
$$B = \frac{U1 - U2}{ln\frac{t2}{t1}}$$

- where U1, and U2 are **the plastic viscosities** of the two down curves, calculated from equation

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

after shearing at a constant rate for **t_1 and t_2 seconds**, respectively.

- **The second** approach is to determine the ***Structural breakdown of a plastic system possessing thixotropy when subjected to increasing shear rates***. (The maximum shear rate is different; the time of holding before reducing shearing stress is constant).
- The principle involved in this approach is two hysteresis loops are obtained having different maximum rates of shear, v_1, and v_2. In this case, a thixotropic coefficient, M, the loss in shearing stress per unit increase in shear rate, is obtained from



$$M = \frac{U1 - U2}{\ln\left(\frac{v2}{v1}\right)}$$

- where M is in dynes sec/cm^2 and U_1, and U_2 are the plastic viscosities for two separate downcurves having maximum shearing rates of v_1 and v_2, respectively.

Negative Thixotropy

- ***Negative thixotropy or antithixotropy***, it is phenomenon represents an increase rather than a decrease in consistency on the downcurve.
- This increase in thickness with increased time of shear was observed in the rheologic analysis of magnesia magma.
- It was detected at shear rates of greater than 30 sec-1; below 30 sec-1 the magma showed normal thixotropy, the downcurve appearing to the left of the upcurve
- Negative thixotropy or antithixotropy **should not be confused with dilatancy or rheopexy**.
- **Dilatant systems** are *deflocculated and ordinarily contain greater than 50% by volume of solid dispersed* phase, whereas **antithixotropic systems** have *low solids content (1%-10%) and are flocculated*.
- **Rheopexy** is a phenomenon in which solid forms a gel more readily when gently shaken than when allowed to form the gel while the material is kept at rest.
- In a **rheopectic** system, the **gel** is the equilibrium form, whereas in **antithixotropy**, the equilibrium state is the **sol**.

Determination of Rheologic Properties

Choice of Viscometer

1. Newtonian Systems

- In a **Newtonian system**, the **shear rate** is directly proportional to **shear stress**.
- This means:
  - If you double the force, the flow rate doubles.
  - The relationship is linear.
  - The viscosity remains constant.
- Because of this simple linear behavior, we can use instruments that operate at **a single shear rate**. These are called **“single-point” instruments**.
- They measure only one point on the rheogram (flow curve).
- From that one point, we can draw a straight line through the origin, and that gives us the complete flow behavior.
- So for Newtonian fluids (like water or simple oils), single-point measurement is sufficient.

Determination of Rheologic Properties

Choice of Viscometer

2. Non-Newtonian Systems

- However, many real materials are **Non-Newtonian**.
- In these systems:
  - Shear stress is NOT directly proportional to shear rate.
  - Viscosity changes with applied force.
  - The flow curve is nonlinear.
- For these materials, a **single-point measurement is virtually useless** Because one point cannot describe a curved relationship.
- Therefore, we need instruments that is Operate at **a variety of shear rates** and Allow us to construct a **complete rheogram**

Determination of Rheologic Properties

Types of Viscometers

- The main instruments used for determining rheological properties are:
  1. **Capillary viscometers**
  2. **Falling-sphere viscometers**
  3. **Cup-and-bob viscometers**
  4. **Cone-and-plate viscometers**
- **Single-shear-rate instruments:**
  - Capillary
  - Falling-sphere
    - These are generally suitable only for **Newtonian materials**.
- **Multiple-shear-rate (rotational) instruments:**
  - Cup-and-bob
  - Cone-and-plate
    - These can be used for:
      - Newtonian systems
      - Non-Newtonian systems
    - Because they allow measurement at different shear rates, they can generate a full rheogram

VISCOELASTICITY

- Viscoelastic measurements are based on the mechanical properties of materials that exhibit both viscous properties of liquids and elastic properties of solids.
- Many of the systems studied in pharmacy belong to this class, examples being creams, lotions, ointments, suppositories, suspensions, and the colloidal dispersing, emulsifying, and suspending agents.

Pharmaceutical areas in which rheology is significant

1. Fluids

a. Mixing
b. Particle-size reduction of disperse systems with shear
c. Passage through orifices, including pouring, packaging in bottles, and passage through hypodermic needles
d. Fluid transfer, including pumping and flow through pipes
e. Physical stability of disperse systems

2. Quasisolids

a. Spreading and adherence on the skin
b. Removal from jars or extrusion from tubes
c. Capacity of solids to mix with miscible liquids
d. Release of the drug from the base

3. Solids

a. Flow of powders from hoppers and into die cavities in tabletting or into capsules during encapsulation
b. Packagability of powdered or granular solids

4. Processing

a. Production capacity of the equipment
b. Processing efficiency