



Physical pharmacy II

lec8

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Rheology

Objective

1-Define rheology, provide examples of fluid pharmaceutical products exhibiting various rheologic behaviors, and describe the application of rheology 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, hysteresis, antithixotropy, rheopexy, plug flow, and viscoelasticity.

3- Define and understand Newton's law of flow and its application.

- The term “rheology,” from the Greek rheo (“to flow”) and logos (“science”), to describe the flow of liquids and the deformation of solids. **Viscosity** is an expression of 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.
- Rheology is involved in the mixing and flow of materials, their packaging into containers, and their removal prior to use, whether this is achieved by pouring from a bottle, extrusion from a tube, or passage through a syringe needle.

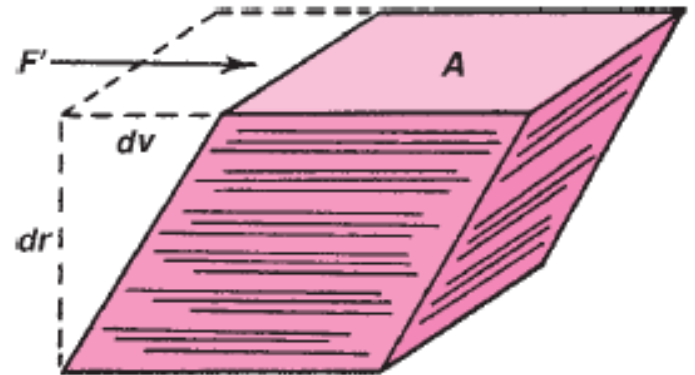
- Rheologic properties of a pharmaceutical system can influence the selection of processing equipment used in its manufacture. Inappropriate equipment from this outlook may result in an undesirable product, at least in terms of its flow characteristics
- When classifying materials according to types of flow and deformation, it is ordinary to place them in one of two categories: Newtonian or non-Newtonian systems. The choice depends on whether or not their flow properties are in accord with Newton's law of flow.

○ Newtonian systems

Newton's Law of Flow

Consider a “block” of liquid consisting of parallel plates of molecules, similar to a deck of cards, as shown in **Figure 1**. If the bottom layer is fixed in place and the top plane of liquid is moved at a constant velocity, each lower layer will move with a velocity directly proportional to its distance from the stationary bottom layer.

Figure 1



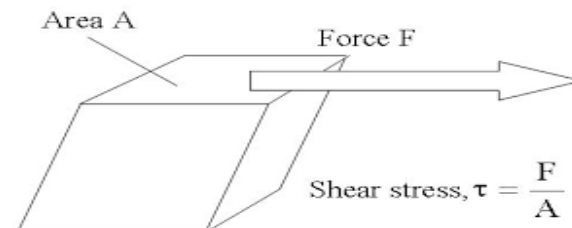
Representation of the shearing force required to produce a definite velocity gradient between the parallel planes of a block of material.

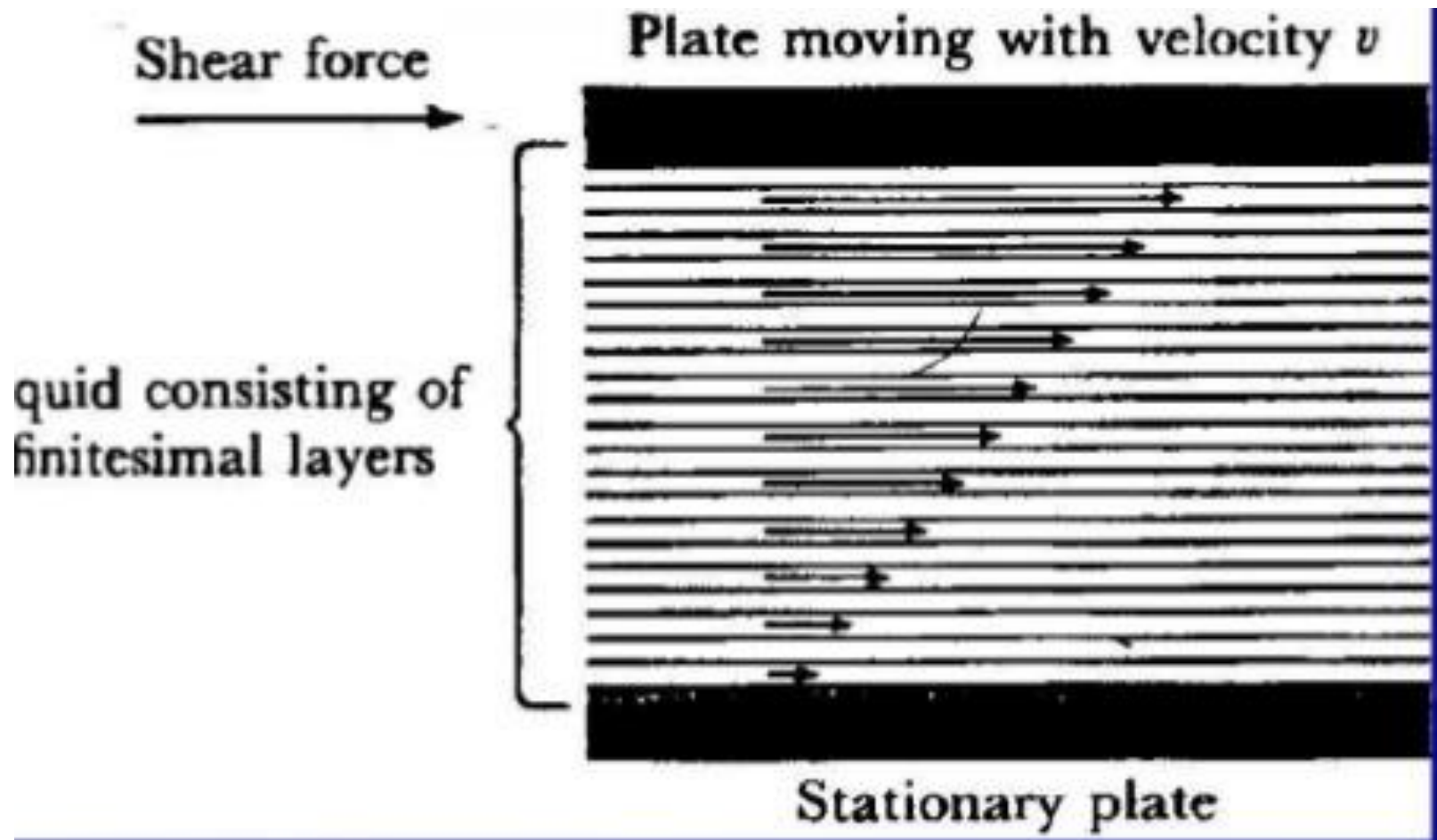
The difference of velocity, dv , between two planes of liquid separated by an infinitesimal distance, dr , is the velocity gradient or rate of shear, dv/dr .

The force per unit area, F/A , required to bring about flow is called the **shearing stress** and is given the symbol F . The viscosity of a liquid, the greater is the force per unit area (*shearing stress*) required to produce a certain rate of shear. **Rate of shear** is given the symbol G . Hence, rate of shear should be **directly proportional** to shearing stress, or

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

Where **eta** (η) is the coefficient of viscosity, usually referred to simply as viscosity, where $F = F/A$ and $G = dv/dr$.





These units are readily obtained by a dimensional analysis of the viscosity coefficient. Rearranging equation

$$\eta = \frac{F' dr}{A dv} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm/sec}} = \frac{\text{dyne sec}}{\text{cm}^2}$$

gives the result

$$\frac{\text{dyne sec}}{\text{cm}^2} = \frac{\text{g} \times \text{cm/sec}^2 \times \text{sec}}{\text{cm}^2} = \frac{\text{g}}{\text{cm sec}}$$

Fluidity, (**phi**) ϕ , a term sometimes used, is defined as the reciprocal of viscosity

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

Examples of Newtonian Fluids:- • Water • Simple Organic Liquids • True Solutions • Dilutes Suspensions • Emulsions

Kinematic Viscosity

Kinematic viscosity is the absolute viscosity, divided by the density ρ (*Rho*) of the liquid at a specific temperature

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

kinematic viscosity ratio of dynamic viscosity to the density of the fluid. The units of kinematic viscosity are the **stoke** (s) and the **centistoke** (cs). Viscosities of some liquids commonly used in pharmacy are given in Table below at 20°C.

**ABSOLUTE VISCOSITY OF SOME NEWTONIAN LIQUIDS
AT 20°C**

Liquid	Viscosity (cp)
Castor oil	1000
Chloroform	0.563
Ethyl alcohol	1.19
Glycerin, 93%	400
Olive oil	100
Water	1.0019

Example

Measuring Viscosity

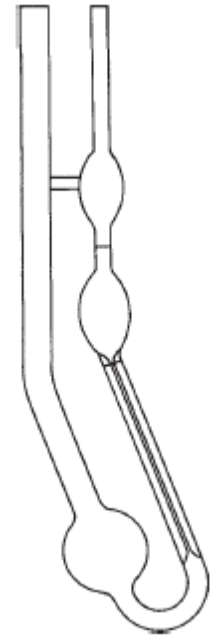
(a) An Ostwald viscometer was used to measure the viscosity acetone, which was found to have a **dynamic viscosity** of 0.313 cp(centipoise) at 25 °C. Its **density** at 25 °C is 0.788 g/cm³. What is the **kinematic viscosity** of acetone at 25 °C?

(b) Water is ordinarily used as a standard for viscosity of liquids. Its viscosity at 25 °C is 0.8904 cp. What is the viscosity of acetone relative to that of water (**relative viscosity, η_{rel}**) at 25 °C?

Solutions:

(a) Kinematic viscosity = $0.313 \text{ cp} \div 0.788 \text{ g/cm}^3 = 0.397 \text{ poise}/(\text{g/cm}^3)$, or 0.397 cs.

(b) $\eta_{rel}(\text{acetone}) = 0.313 \text{ cp}/0.8904 \text{ cp} = 0.352$
dimensionless



Ostwald–
Cannon–Fenske
viscometer

○ **Non-Newtonian Flow**

Non - Newtonian bodies are those substances, which fail to follow Newton's law i.e. liquid & solid , heterogeneous dispersions such as colloidal solutions, emulsions, liquid suspensions and ointments.

Non-newtonian fluids The fluid which do not obey Newton Law's they are termed as Non-Newtonian Fluids. Types of Non-Newtonian Fluids:-

☐ Time Dependent

- Thixotropy e.g lotions, gels, ketchup, paints ,
- Rheopexy e.g gypsum pastes and printer inks

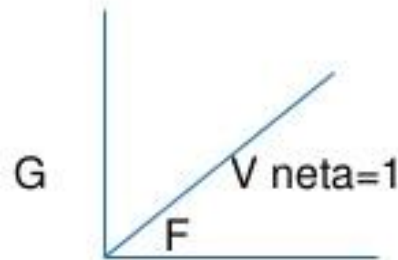
☐ Time Independent They are classified into 3 types of flow:

- Plastic flow.
- Pseudoplastic flow.
- Dilatant flow e.g corn starch in water

Thixotropy

- **Thixotropy** is **defined** as the progressive decrease in viscosity with time for a constant applied shear stress, followed by a gradual recovery when the stress is removed.
- **Thixotropy** is a time-dependent shear thinning property. Certain gels or fluids that are thick or viscous under static conditions will flow (become thinner, less viscous) over time when shaken, agitated, shear-stressed, or otherwise stressed (time dependent viscosity).
- **Antithixotropy**: This is also called as negative thixotropy, this represents an increase in consistency on the down curve. The down curve shifts to the right of the up curve. This is also called as sol to gel to sol transformation
- **Rheograms**
A *rheogram* is a plot of *shear rate*, G , as a function of *shear stress*, F . Rheograms are also known as consistency curves or flow curves. The rheologic properties of a given material are most completely described by its unique rheogram

Rheogram

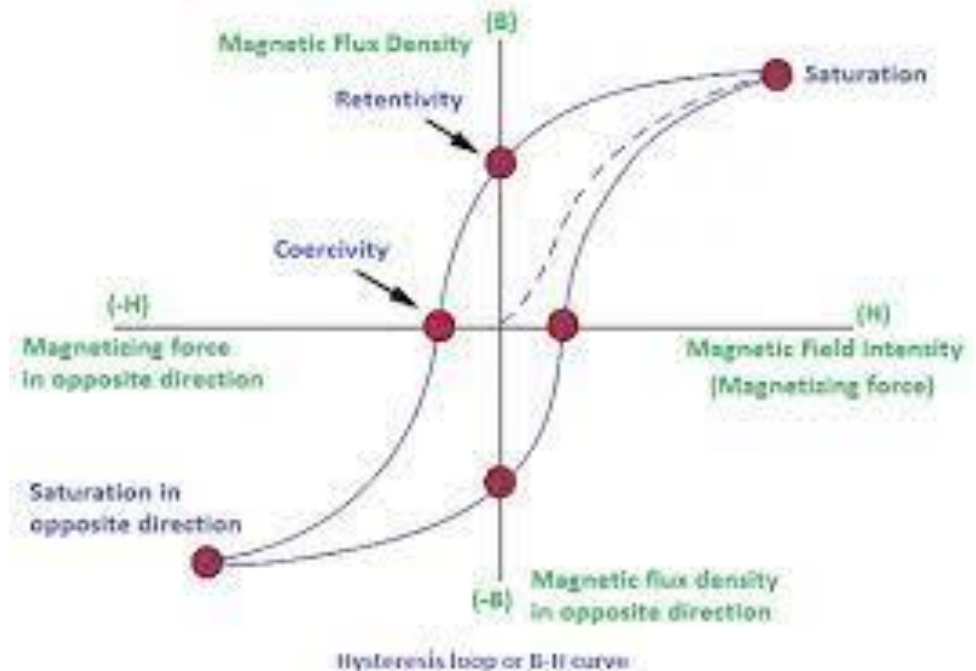


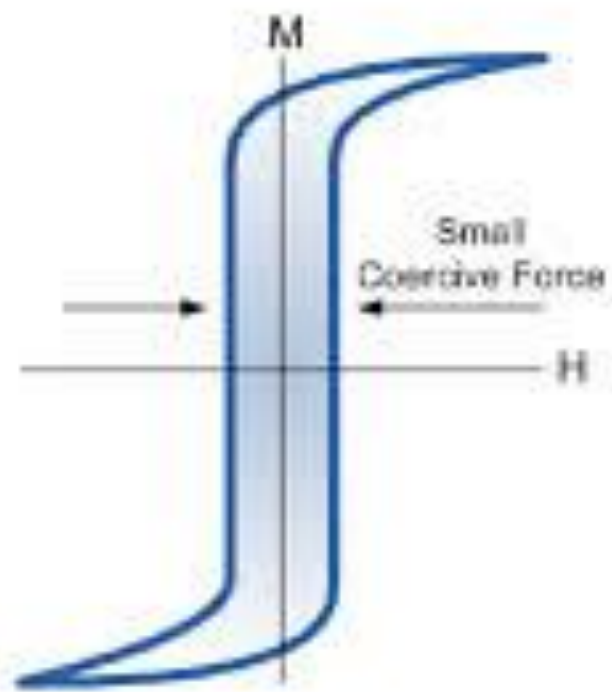
Rheogram: Rheogram is a plot of rate of shear Vs shearing stress. For Newtonian liquid if G is plotted Vs F the flow curve gives straight line passing through the origin and the slope is the coefficient of viscosity and is equivalent to 1

Measurement of Thixotropy

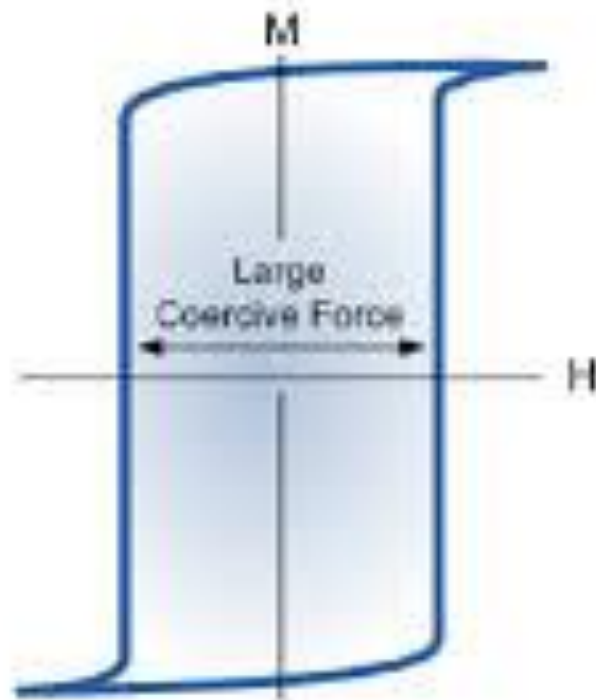
A quantitative measurement of thixotropy can be attempted in several ways. The most apparent characteristic of a thixotropic system is the **hysteresis loop** formed by the upcurves and downcurves of the rheogram. This area of hysteresis has been proposed as a measure of thixotropic breakdown; it can be obtained readily by means of a planimeter or other suitable technique

hysteresis loop





Soft iron

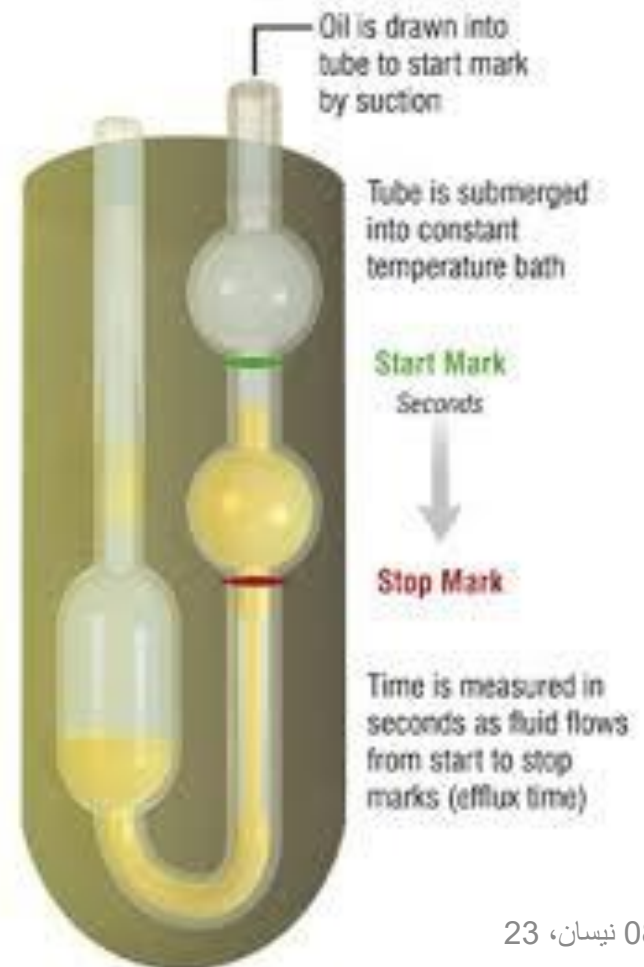


Hardened steel

Choice of Viscometer

A **viscometer** (also called viscosimeter) is an instrument used to measure the viscosity of a fluid. For liquids with viscosities which vary with flow conditions,

- ✓ "One point" instruments :
- ✓ Multi-point" instruments:
- ✓ Falling Sphere Viscometer
- ✓ Cone and Plate Viscometer



Thixotropy in Suspension and Emulsion Formulation:

- Thixotropy is useful in the formulation of pharmaceutical suspensions and emulsions. They must be poured easily from containers (low viscosity)
- **Disadvantages of Low viscosity:**
 - ✓ Rapid settling of solid particles in suspensions and rapid creaming of emulsions.
 - ✓ Solid particles, which have settled out stick together, producing sediment difficult to redisperse ("caking or claying").
 - ✓ Creaming in emulsions is a first step towards coalescence. (break down of emulsion)

