MODULE 2: Rheology

Lecture 2

Name of the Faculty: Dr. Shikha Srivastava

DISCLAIMER

All the content material provided here is only for teaching purpose

5. NON-NEWTONIAN SYSTEMS

Most pharmaceutical fluids do not follow Newton's equation:

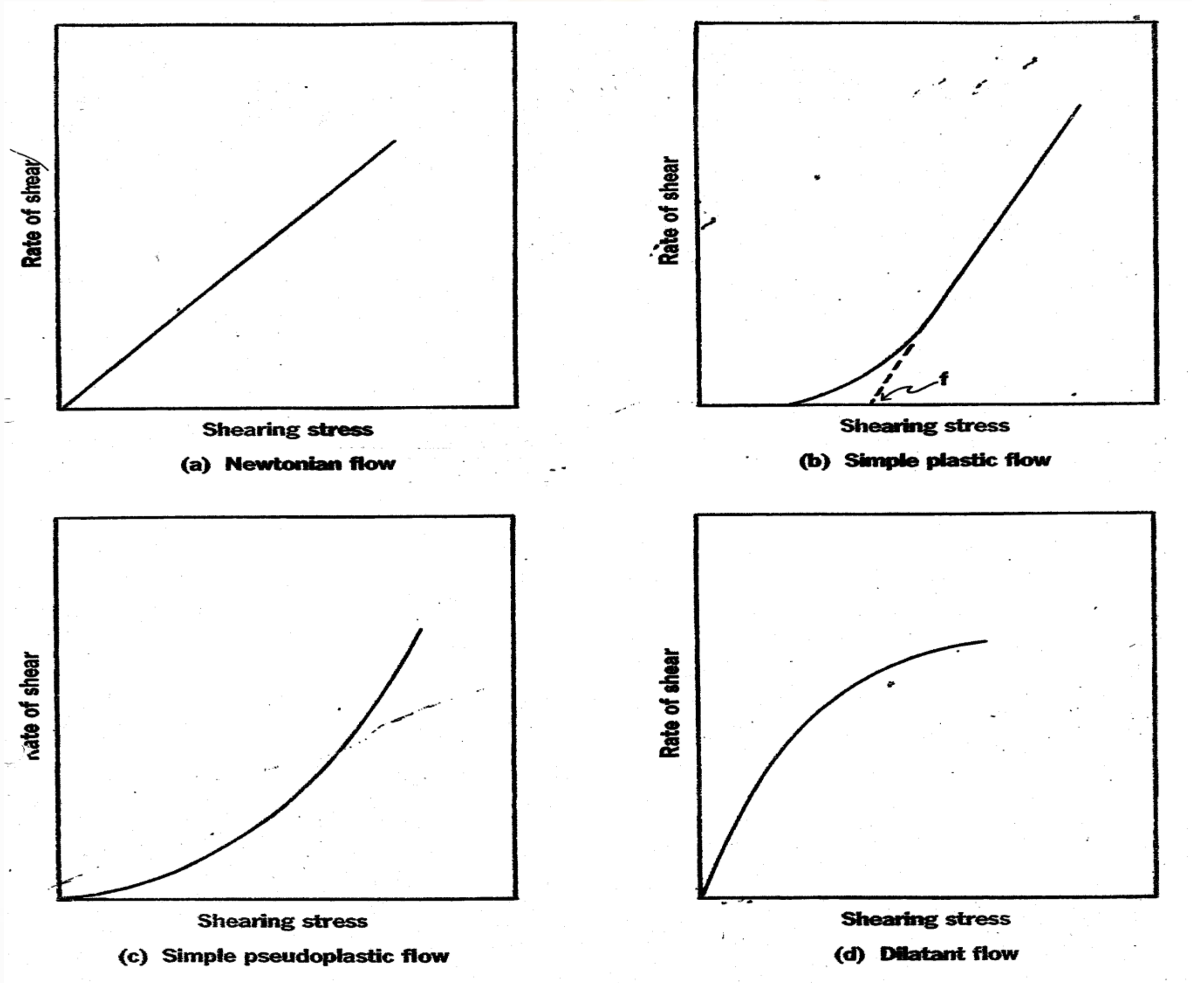
- because the viscosity of fluid varies with the rate of shear.

- therefore a single determination of viscosity at any one rate of shear cannot yield the entire rheological profile.

- i. Plastic or Bingham flow
  ii. Pseudoplastic flow
  iii. Dilatant flow

Rheograms for Newtonian and Non-Newtonian Flow

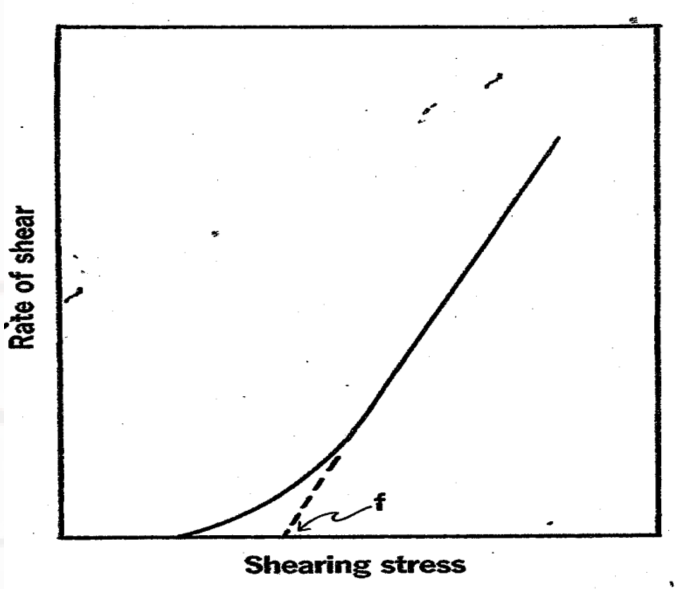
Physical Pharmacy p.522



5.1 Plastic or Bingham flow

- The rheogram does not pass through the origin.
- Intersects with the shear stress (x) axis .

  (or will if the straight part of the curve is extrapolated to the axis)
- X - intercept is usually referred to as the ***yield*** value.



(b) Simple plastic flow

- A Bingham body does not begin to flow until a shearing stress, corresponding to the yield value, is exceeded.

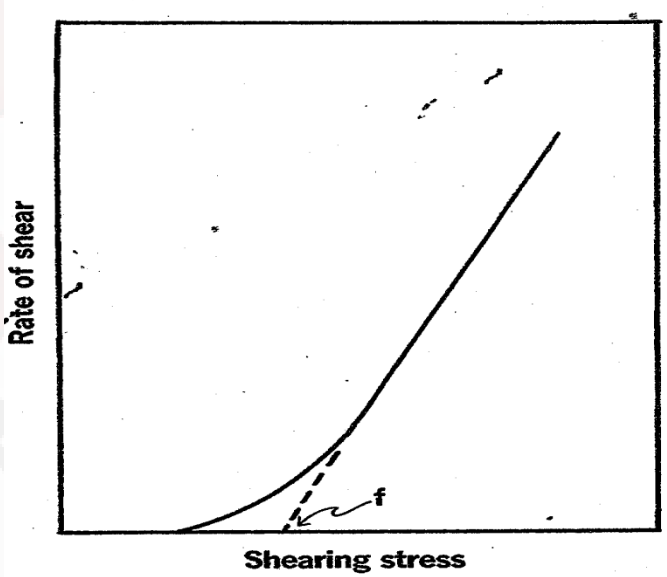
- If stress is less than the yield value, the system behaves like a solid and exerts elastic deformations that are reversible.

- The quantitative behaviour of these bodies is best described by the Bingham Equation where f_B is the Bingham yield value:

Newtonian $S = \eta \cdot dv/dx$

$$\eta = \frac{S}{dv/dx}$$

Non-Newtonian $$\eta_{pl} = \frac{S - f_B}{dv/dx}$$



(b) Simple plastic flow

- In practice, **deformation and flow** usually occurs at a **lower shear stress** value and this accounts for the **curved portion** of the curve.

- The **viscosity decreases initially** and then remains **constant**.

- In a **highly flocculated system**, there is interaction between flocs which results in a **structured system** and **plastic flow** is associated with these systems ***e.g highly flocculated suspensions.***

- The yield value is present because of the **contacts between adjacent particles** (caused by van der Waals forces which may be capable of withstanding weak stresses) which must be **broken down before flow** can occur.

- Consequently, the **yield v**alue is an indication of the **degree of flocculation**; the more flocculated the suspension, the higher will be the yield value.

- This type of behaviour is also exhibited by ***creams and ointments.***

5.2 Pseudoplastic flow

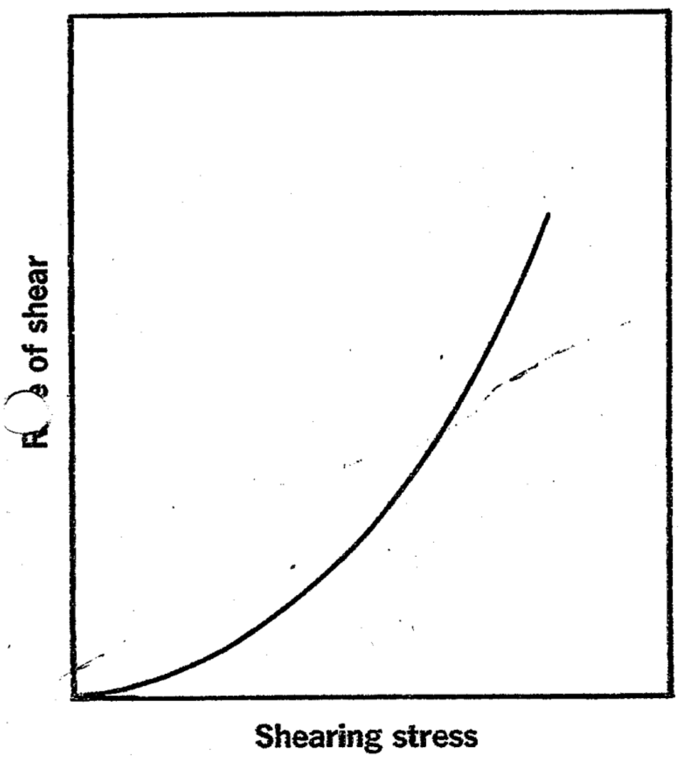
- Many pharmaceutical products exhibit ***pseudoplastic flow*** include natural and synthetic gums

  e.g. liquid dispersions of tragacanth, sodium alginate, methylcellulose, sodium carboxymethylcellulose,.

- As a general rule:

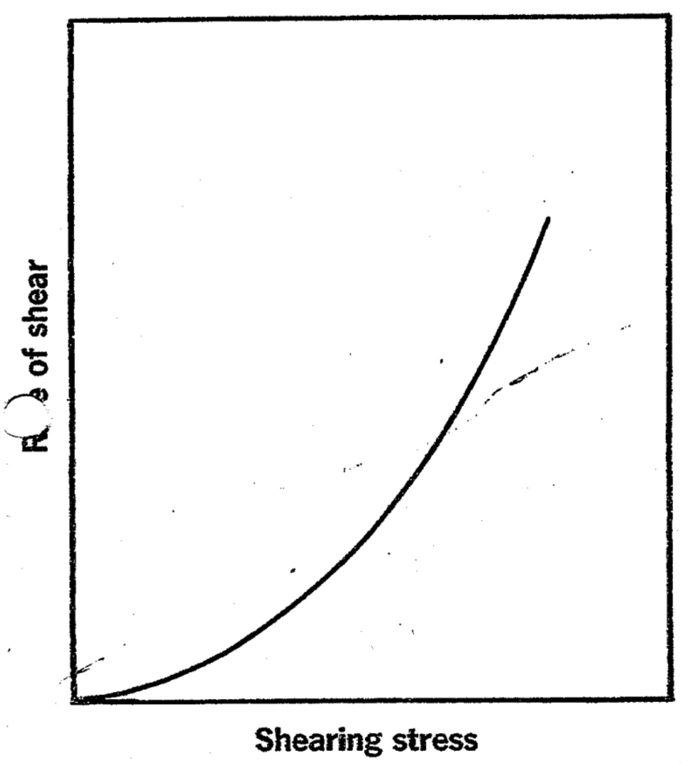
  Pseudoplastic flow is exhibited by polymers in solution

  Plastic systems are composed of flocculated particles.



(c) Simple pseudoplastic flow

- The curve commences at the origin and there is no yield value.
- No part of the curve is linear, so viscosity cannot be expressed by any single value.
- The apparent viscosity may be obtained at any rate of shear from the slope of the tangent to the curve at the specified point.
- The viscosity decreases with an increasing rate of shear (shear-thinning systems).



(c) Simple pseudoplastic flow

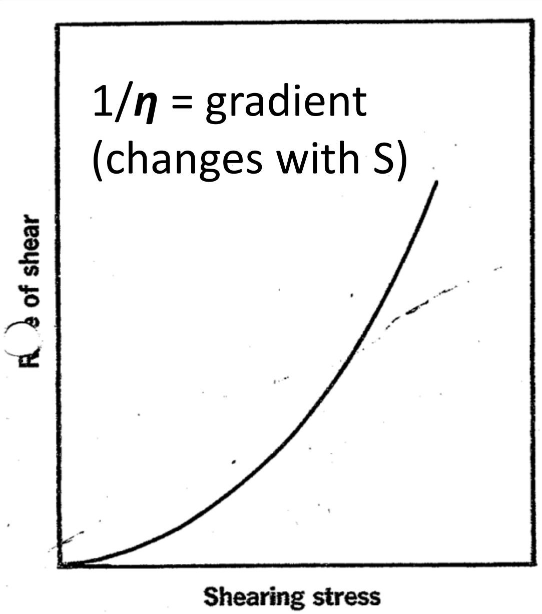
- Pseudoplastic flow cannot be satisfactorily expressed by fundamental equations.

- The following empirical equation correlates most closely with experimentally observed flow not involving stress over vast ranges:

$$S^n = \eta^1 \frac{dv}{dx} \qquad n > 1 ; \qquad \text{the term } \eta' \text{ is a viscosity coefficient.}$$

- The exponent ***n*** rises as the flow becomes increasingly non-Newtonian.

- When $n = 1$, this equation reverts to the classic Newton equation and the flow is Newtonian.



(c) Simple pseudoplastic flow

At the Particulate level:

- The curved rheogram for pseudoplastic materials results from a shearing action on the long-chain molecules which become entangled and associated with immobilized solvent.

- As the shearing stress is increased, the randomly arranged particles tend to become disentangled and align their long axes in the direction of flow.

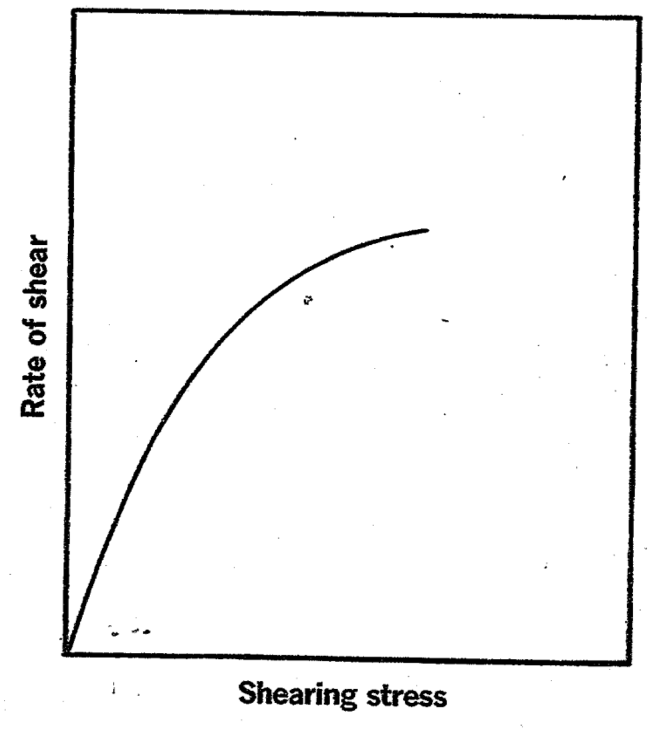
- This orientation reduces the internal resistance of the material and offers less resistance to flow. Some of the entrapped water will also be released.

- Both of these account for the lower viscosity. Once stress is removed, the structures reform spontaneously.

5.3 Dilatant flow

- Dilatant flow - usually ***suspensions containing a high concentration (>50%) of small, deflocculated particles***.
- Exhibit an increase in resistance to flow with increasing rates of shear.
- Systems increase in volume when sheared - termed ***dilatant***.
- The reverse of pseudoplastic systems.
- Pseudoplastic systems – ***shear-thinning systems***,

Dilatant materials - ***shear-thickening systems***.



(d) Dilatant flow

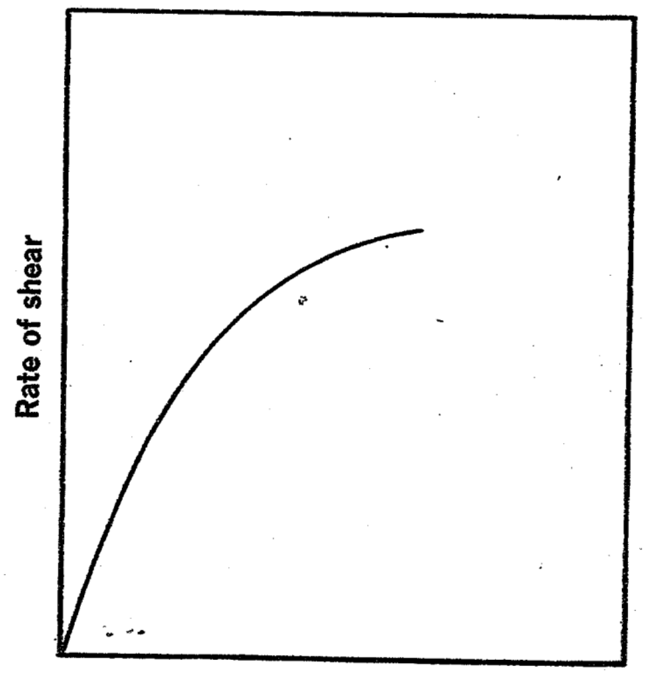
- The same equation can be used to describe dilatancy in quantitative terms:

$$S^n = \eta^1 \frac{dv}{dx} \qquad n < 1$$

- n is always less than 1

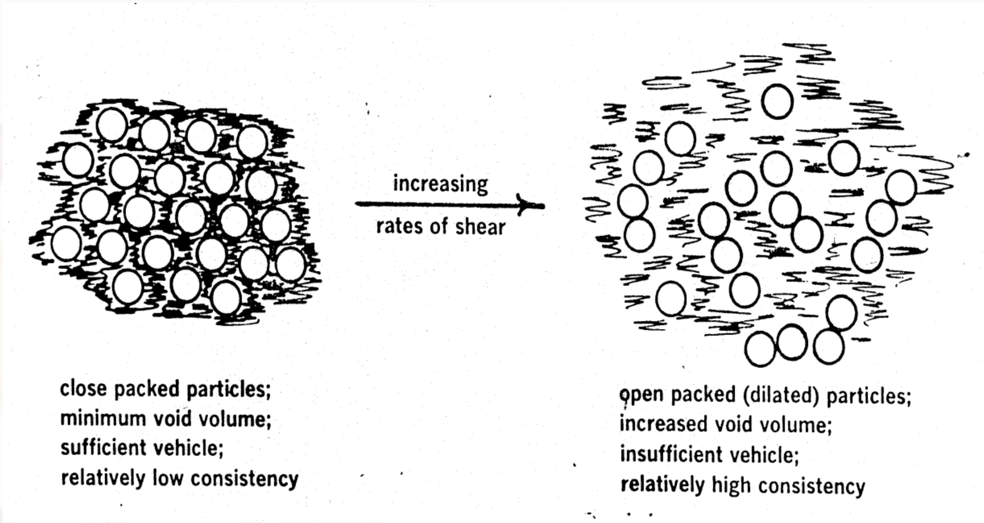
- Decreases as the degree of dilatancy increases.

- As n approaches 1, the system becomes increasingly Newtonian in behaviour.



(d) Dilatant flow

At the particulate level:



- At rest:
  - particles closely packed
  - voids at a minimum.

- Vehicle:
  - sufficient to fill this volume
  - allows the particles to move relative to one another at low rates of shear.

- Can pour a dilatant suspension from a bottle without shaking as it is relatively fluid without shear stress applied.

- If the shear stress is increased by shaking, the bulk expands or dilates as the particles move quickly past each other and take an open form of packing.

- Such an arrangement results in a significant increase in the void volume, with the vehicle now being insufficient to fill the voids between the particles.

- The resistance to flow increases since the particles are no longer completely wetted or lubricated by the vehicle and eventually the suspension will set up as a firm paste.

- Caution must be taken in processing dilatant materials.
  - Usually, the processing of dispersions containing solid particles is facilitated by the use of high speed mixers, blenders or mills.

  - Dilatant materials may solidify under these conditions of high shear, thereby overloading and damaging the processing equipment.

6. THIXOTROPY

6.1 Description

- So far for Newtonian and non-Newtonian behaviour:
  - observed behaviour when the rate of shear was progressively increased and plotted against the resultant shear stress.

- Assumed that if the rate of shear was reduced, the down-curve would be identical with and superimposed on the up-curve.

- This is so with -Newtonian systems
  -some non-Newtonian materials.

- For **most non-Newtonian systems**:
  - The flowing elements, whether particles or macromolecules, may not adapt immediately to the new shearing conditions.
  - When subjected to a particular shear rate, the shear stress and consequently the viscosity, will decrease **with time**.
  - Therefore the down-curve can be displaced with regard to the up-curve.

- **Thixotropic systems** usually contain **asymmetric particles** and through numerous points of contact, these particles set up a loose **3-D network** throughout the sample.

- **At rest**, this structure confers **some degree of rigidity** on the system, and it resembles a **gel**.

- **As shear is applied** and flow starts, this **structure begins to break down** as the points of contact are disrupted and the particles become aligned in the general direction of flow.

- The **material undergoes a gel to sol transformation** and exhibits **shear thinning**.

- Upon **removal of the stress**, the structure starts to **reform**. This is not instantaneous, but is a **progressive restoration** of consistency as the asymmetric particles come into contact with each other by undergoing random Brownian movement.

- ***Shear-thinning systems (plastic and pseudoplastic***)
- - down-curve is frequently displaced to the left of the up-curve
- - rheogram exhibits a hysteresis loop.

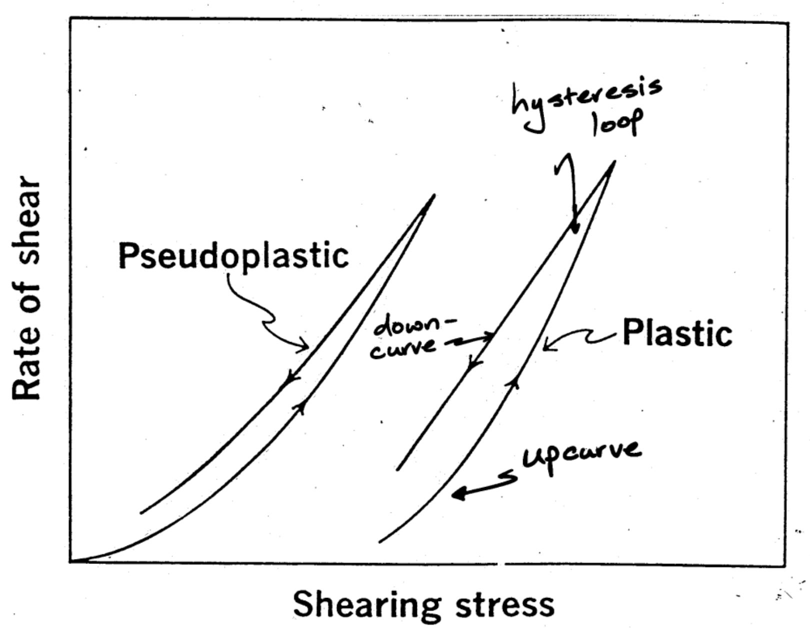


FIG. 19-4. Thixotropy in plastic and pseudoplastic flow systems.

- i.e. the material has a lower consistency at any one rate of shear on the down-curve than it had on the up-curve.

- Indicates a breakdown of structure that does not reform immediately when the stress is removed.

- This phenomenon is known as thixotropy and may be defined as:
- “A**n isothermal and comparatively slow recovery, on standing of a material whose consistency is lost through shearing**".

- According to this definition, thixotropy can **only** be applied to shear-thinning systems.

- The rheograms obtained with thixotropic materials are:

- highly dependent on the **rate** at **which shear is increased or decreased**

  - **the length of time** a sample is subjected to any one rate of shear.

6.2 Measurement of thixotropy

- Main characteristic of a thixotropic system is the hysteresis loop.

- The area of hysteresis has been proposed as a measure of thixotropic breakdown.

- Two approaches:

  - determine the structural breakdown with time at a constant rate of shear.
  - determine the structural breakdown due to increasing shear rate.

- Limitations:
  - Does not taken into account the shape of the up- and down-curves. So
  - Two different materials may produce loops of similar area but which have completely different shapes representing totally different flow behaviour.

- **Rheogram of white soft paraffin**

This is typical of a loop obtained with some samples of white soft paraffin where the up-curve exhibits a number of bulges.

- **Lower shear rates**

the bulges are thought to be associated with the initial loss of 3-D structure.

- **Higher shear rates**

the smoother deviations here are associated with molecular reorientation.

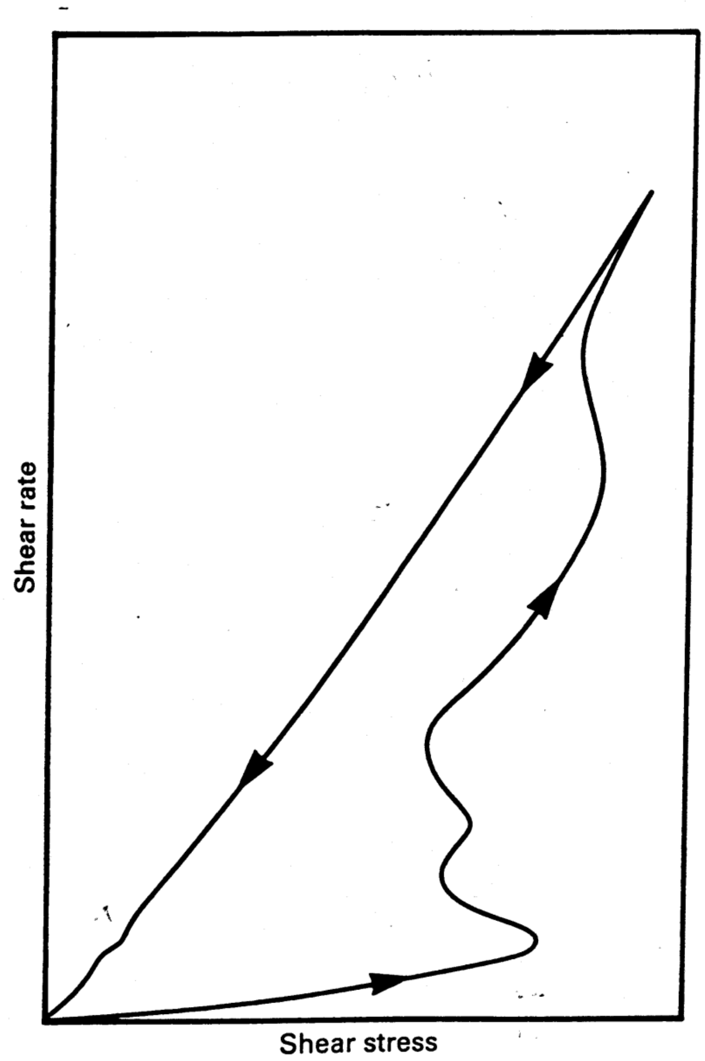


Fig. 2.12 Complex rheogram produced by a pharmaceutical gel

6.3 Rheopexy

- This is a characteristic exhibited by **some thixotropic systems**.
- A phenomenon where a **sol forms a gel** more readily **when gently shaken** than when allowed to form the gel while the material is kept at rest.
- The rocking motion provides a mild turbulence which aids in returning de-randomised particles to a random orientation.
- The **gel** is the **equilibrium form**.

6.4 Thixotropy in formulation

- **Thixotropy is a desirable property** in liquid pharmaceutical systems that ideally should have:
- **A high consistency** in the container **yet pour or spread easily**.
- e.g.
- a well formulated suspension will not settle out readily in the container
- will become fluid on shaking and will remain so long enough for a dose to be dispensed.
- will regain consistency rapidly enough so as to maintain the particles in a suspended state.

- Also desirable with emulsions, lotions, creams, ointments and parenteral suspensions to be used for intramuscular depot therapy.

8. DETERMINATION OF RHEOLOGIC PROPERTIES

8.1 Why measure viscosity?

-Formulation development	Quantities of ingredients Grades of ingredients Formulation requirements Production Methods - mixing rate - temperature Setting limits for production
- Production	Quality Assurance / Batch-to-batch uniformity ? Production methods - variability ? Adjustments to formulation - thicken ? Quality of ingredients – natural products vary

- Other rheologic properties:
  - tackiness or stickiness
  - "body”
  - "slip“
  - "spreadability"

- Are difficult to measure by means of a conventional apparatus and do not have precise meanings.

8.2 Pharmaceutical Considerations and Applications

- **Problems in establishing meaningful shear rates**

  Viscosity requirements often **emperical**, however, researchers have attempted to establish shear rates relating to the use of pharmaceuticals e.g.

  - topical application - 120 sec^{-1}

  - nasal spray in a plastic squeeze bottle - 1000 sec^{-1}

  - pouring from a bottle - below 100 sec^{-1}.

- However, think about the shear rate resulting from rubbing a cream into the skin. This can range from 100 to 10 000 sec^{-1} depending on the degree of rubbing. The shear rate for individual use by a process therefore varies greatly.

- Another example is squeezing a product from a collapsible container - the shear rate depends on the squeezing force that the subject can exert easily.

- **Visual perception**
- The importance of viscosity in visual perception must be considered e.g.cream to hold its shape in a jar a lotion to pour a toothpaste to retain its ribbon shape on a brush.
- Here shear rate is determined by subjectively evaluating an acceptable rate of deformation or flow under the constant stress of gravity.

- ***Ease of use***
- e.g. Toothpaste.
- After applying a rate of shear in squeezing the tube, the toothpaste must flow onto the bristles.
- It must then recover its viscosity sufficiently to maintain its ribbon shape on the brush.
- With shear, it must thin rapidly for ease in brushing.

- **Topical preparations must meet certain criteria for:**
  - Desirable pharmaceutical properties
    feel, spreadability, colour, odour
  - Desirable pharmacological properties – drug release

- **Other psychologic and sensory characteristics e.g.**
  - Sensations in the mouth
  - Between the fingers
  - On the skin

  are important considerations for manufacturers of cosmetic products and dermatologic products.

- Cussler et al studied the texture of non-Newtonian liquids of widely different rheologic properties applied to the skin.

  Found that the consistency of the material could be accurately assessed by a panel of untrained subjects by the use of only 3 attributes:

  - thinness - related to non-Newtonian viscous parameters that could be measured with appropriate instrumentation

  - smoothness - related to the coefficient of friction

  - warmth - complex concept that requires further study.

  Only 1 of these can be reliably measured – the rest are largely subjective.

- **It can therefore be seen why statement defining a suitable viscosity for products are meaningless unless they are framed within a specific judgement of use.**

- **Product development**

  In product development it is vitally important that all trial formulations be tested:

  - against assumed stresses and shear rates likely to be experienced in manufacturing, product movement, filling and use.

  - These values must be calibrated, preferably with products characteristically used and under the normal operating parameters of that facility.