

Introduction to Rheology

Rheology is the study of the flow and deformation of matter from solids to gases. It describes the relationship between force, deformation and time. It comes from the Greek "rheos" that means to flow.

The consistency of different products describes fluid rheology. Fluid rheology is studied by viscosity (η) and elasticity. Viscosity is the resistance to flow and elasticity is usually stickiness.

Common to liquids, solids and substances in between the former two is that if a stress is applied to them, they will strain. Stress may be visualized by placing a small amount of fluid between two parallel plates. When one plate slides over the other, forces act on the fluid dependent upon the rate of the plate movement. This causes a shear stress on the liquid. Recall laminar flow of fluids through a tubular vessel. Strain is the response to the stress. If solids are elastic, they deform and return to their original shape. Since fluids are not elastic and, hence, viscous, their deformation is irreversible.

For practical purposes, there are three types of fluids:

Newtonian Fluids	Non-Newtonian Fluids, Time INdependent	Non-Newtonian Fluids, Time DEpendent
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The viscosity of Newtonian fluids is dependent only on temperature. Examples of Newtonian fluids are water, milk, sugar water, mineral oil, ethyl alcohol.

The viscosity of non-Newtonian time Independent fluids is dependent on temperature and shear rate. The flow behavior of these fluids may be classified as follows:

Shear Thinning	Shear Thickening	Plastic
aka: pseudoplastic	aka: dilatant	aka: Bingham Plastic Fluid
Viscosity goes down with increased shear rate	Viscosity increases with increased shear rate	Requires a threshold shear stress before flow occurs -- this is called a yield value
E.g., paint, shampoo, ketchup, fruit juice concentrates	E.g., wet sand, concentrated starch suspensions	E.g., tomato paste, tooth paste, hand cream, grease

The viscosity of non-Newtonian time dependent fluids is dependent on temperature, shear rate and time. There are 2 classifications of these fluids:

Thixotropic	Rheopectic
Common in the food and chemical industries	Very rare
Time thinning	Time thickening
Viscosity goes down with time	Viscosity increases with time
E.g., yogurt, paint	E.g., gypsum paste

All materials from gases to solids can be classified into 4 groups by rheological behavior:

Viscous	Viscoelastic	Elasticoviscous	Elastic
<p>All energy added is dissipated into heat</p> <p>E.g., water</p>	<p>Materials appear solid</p> <p>With stress causes a non-instantaneous deformation that is incompletely irreversible</p> <p>Stores some energy and flows a little with deformation</p> <p>E.g., bread dough, polymer melts, gels, glass window</p>	<p>Materials appear liquid</p> <p>With stress causes indefinite deformation</p> <p>With release of deforming stress, recovers some shape</p>	<p>All energy added is stored in the material</p>

Arithmetically and graphically, we can examine Newtonian and the two non-Newtonian fluids. For Newtonian fluids, the stress-strain relationship is linear (of the form $y = mx + b$ that you studied in high school algebra) and fits the following equation:

$$SS = \eta * SN$$

Where SS is the shear stress, η is the viscosity and SN is the shear strain. Graphically, it fits the following general type of curves,



Figure 1.

The viscosity (slope of the line) is a constant regardless of the shear stress and independent of time. Gas and some liquids (water) approximate Newtonian behavior

Non-Newtonian time-independent fluids share the stress-strain relationship (strain is a function of stress and nothing else) with a few modifications. The first fluid in this category we'll examine is the Bingham plastic fluid. These fluids collapse above a threshold stress followed by linear rheological behavior. The equation for the Bingham fluid is:

$$SS = SS_0 + \eta * SN \text{ and } SS > SS_0$$

This fits the following general type of curve,

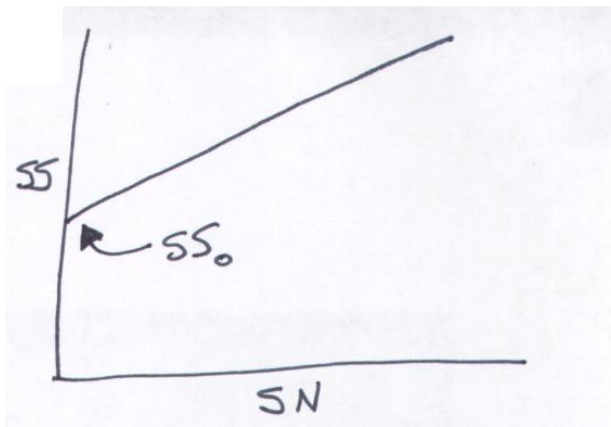


Figure 2

Examples of Bingham fluids include coal suspensions, latex paint and painter's ink.

The second category of these fluids is the pseudoplastic. Although they have no threshold stress, SS increases exponentially with SN. This fluid may be studied by the following equation:

$$SS = K * SN^x$$

K and x are constants. The pseudoplastic fluid follows the curve in

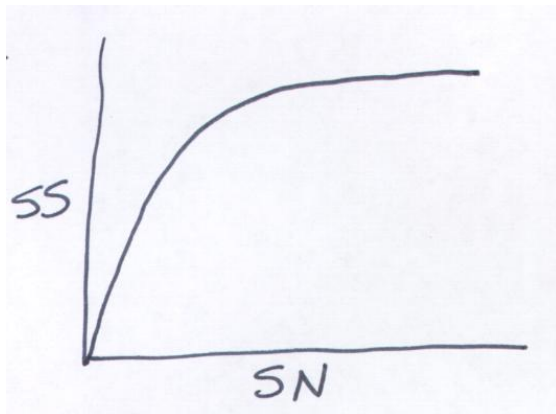


Figure 3

Because of the equation used to describe these fluids, pseudoplastics are also called "power law" fluids. In the case of a pseudoplastic, x is ALWAYS < 1.

As the SS in the pseudoplastic increases, note that the slope decreases. This means that the apparent viscosity (coming up in a bit) decreases with increasing SS. Pseudoplastic fluids are also called shear thinning fluids.

If incomplete data is taken on a pseudoplastic, it could appear to be either Newtonian or Bingham by extrapolation,

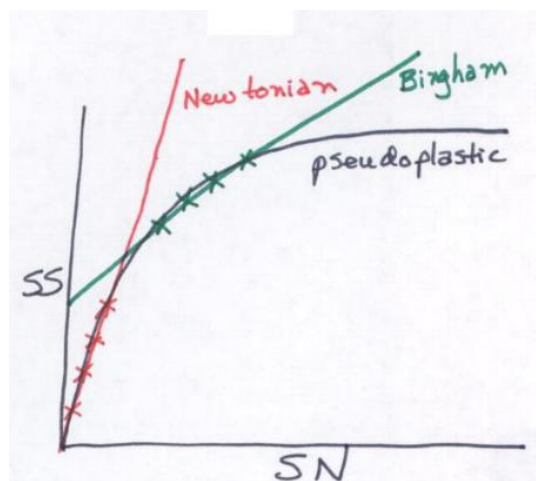


Figure 4

The 3d category of non-Newtonian time independent fluids is the dilatant fluids. They, too, obey the power law except that x is always > 1 . The curve is as appears in

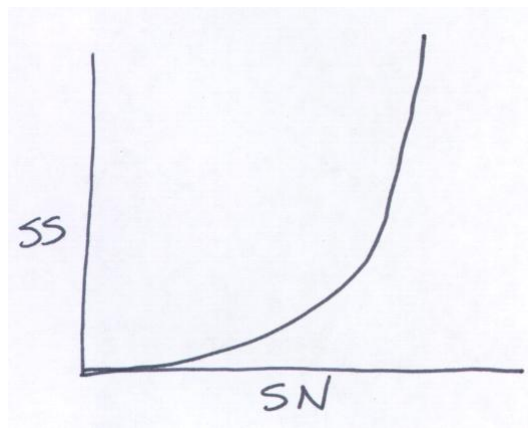


Figure 5

Note that the slope increases with increasing SS. This means that the apparent viscosity is increasing. These fluids are also called shear thickening. PVC pastes are often dilatant. Since these fluids vary exponentially, it is possible for them to be dilatant over one range of shear rates and pseudoplastic over a different range of shear rates. The other name for these two fluids that obey the power law is Ostwalde-de Waele fluids.

Note that there is no proportionality constant between SS and SN, hence η as we discussed with Newtonian fluids does not exist with power law fluids. It is more common to use the term apparent viscosity, defined as SS/SN .

The Measurement of Viscosity

Instruments used to measure viscosity, η , are called viscometers or viscosimeters if they measure shearing viscosity. The oscillating type is generally called a rheometer. They may be as simple as Ostwald viscometers you'll use in the lab or as complex as a conical cup with a bob.

There are at least 4 methods available by which to determine viscosities: falling ball, open tube, conical cup and harmonic deformation.

The open tube is what you will use in the lab. It is not the method of choice in industry or research, but nevertheless provides suitable basic science application of studying viscosity.

The falling ball method is acceptable for crude determination. In general, the fluid is poured into a tube with a ball. The tube is inverted and the time it takes for the ball to pass between two marks is measured. The time is compared to a chart to get the viscosity.

The conical cup with fluid in the space between cup and rotor/impactor provides the foundation of most research viscometry. In this method, the rate of shaft rotation or the applied torque is measured via computer interface/application, e.g., a Brookfield viscometer,



Figure 6

Rotating viscometers measure shear. Data obtained from different torques would help determine the SS_0 of, e.g., catsup, i.e., when it would begin to flow.

An unusual variation of the Brookfield viscometer (which utilizes varying torques) is to measure constant torque in non-Newtonian fluids that have their viscosities dependent on time. The data obtained may show creep. Creep is defined as change with time.

The fourth method, harmonic deformation, may be used to determine viscoelasticity. The difference in this method is that instead of continuous cup rotation, the cup is moved back-n-forth in a sinusoidal motion. The motion is set so as to not break the sample, yet stress it.

A completely elastic gel would show the bob moving in phase with the cup. If the substance was a fluid, the bob would move out of phase with the cup. Materials that are viscoelastic move partly out of phase.

The phases are recorded by a pen on the "torque bar" and on the cup on a chart recorder,

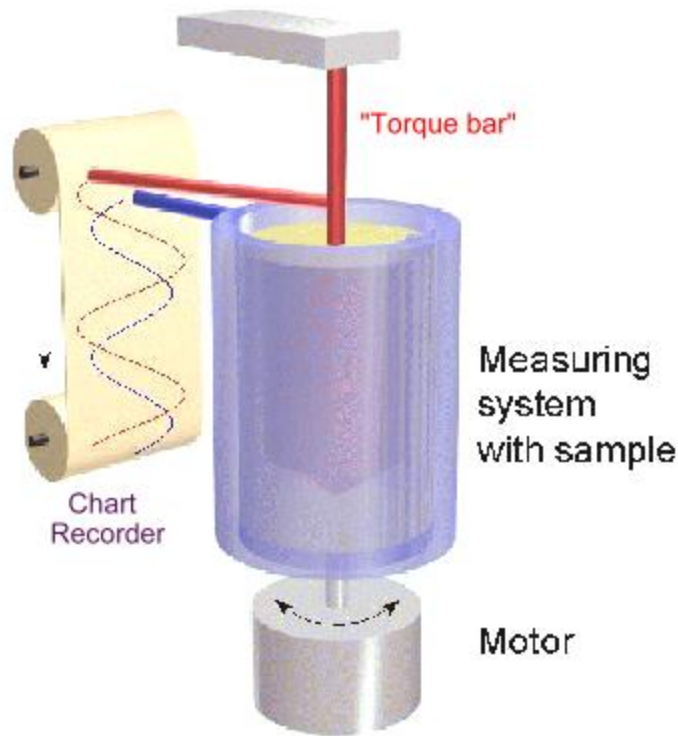


Figure 7

The remainder of viscometry measurements will be covered, below, in the lab experiment for viscometry.

Experimental Viscometry

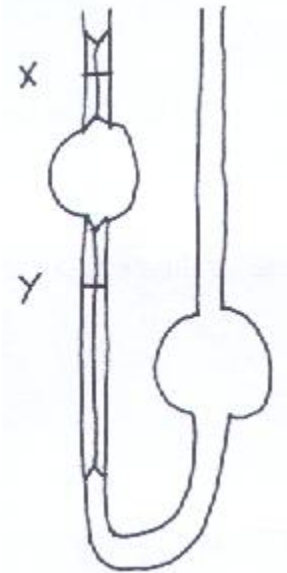
Introduction

A physical property of liquids that is easily measured in the laboratory is the viscosity of liquids. Viscosity is the measure of the ease in which a liquid flows through a tiny capillary tube, i.e., sort of how "sticky" it is. Typically it is measured in reference to another liquid. When the viscosity of blood is compared to the viscosity of water, for example, blood turns out to be 4-5 times as viscous as water -- in other words, it flows at 1/4 to 1/5 the rate of the flow of water.

There are a number of methods with which to measure viscosity of liquids. The method employed in this experiment utilizes Ostwald's viscometer:



In this method, a pipet bulb is placed over the right arm of the viscometer and air is blown through the glass tubing to move the liquid above point "X".



After the liquid is above point "X", the bulb is withdrawn. When the liquid flows to point "X", the time necessary for it to flow to point "Y" is measured and recorded in seconds.

Prior to getting into the derivation of the necessary equations for determining the viscosity of your sample liquid, there are some variables it is necessary to be familiar:

η = viscosity of the liquid in millipoise

C = the calibration constant of the viscometer and must be determined for each viscometer

ρ = the density of the liquid in g/mL; for water, we assume it is 1 g/mL

Δt = the time for the liquid to flow between points "X" and "Y" in seconds

To calculate the viscosity, then, the following equation is used:

$$\eta = C \rho \Delta t$$

The calibration constant, though, must be determined experimentally and then calculated:

$$C = \frac{\eta_o}{\rho_o \Delta t_o}$$

Where the subscript "o" for viscosity and density mean that these values are from a table of GIVEN values for the given liquid (water in this case) and the Δt is the time in seconds in which the liquid (in this case, water) flows between the points "X" and "Y".

The experimentally determined viscosity of a liquid may then be calculated by combining the previous two equations where the second equation substitutes for "C" in the first equation to give:

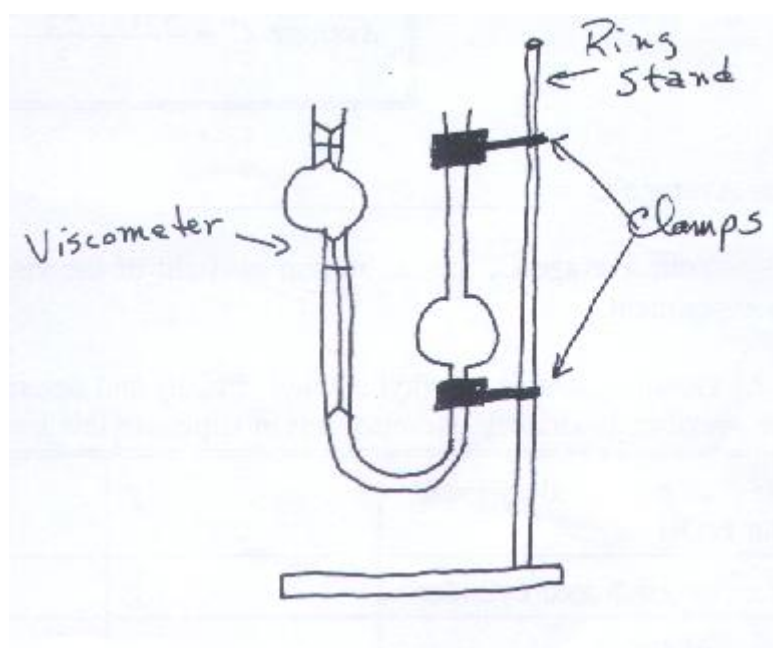
$$\eta = \frac{\eta_o \rho \Delta t}{\rho_o \Delta t_o}$$

The table, below summarizes sample viscosities of commonly used laboratory liquids at 20°C. Note that, as intuitively determined, glycerol is almost 7 times as viscous as water.

Sample viscosities of typical laboratory reagents at 20°C. Source: Dodd, R.E. and Robinson, P.L.: Experimental Inorganic Chemistry . (Elsevier: Amsterdam) © 1957, pp. 367-9.	
Liquid	Viscosity, η , millipoise
Acetone	3.29
Water	10.08
Ethyl alcohol	12.0
Glycerol	66.2

Method

Obtain as a group (pairs) an Ostwald viscometer, ring stand, pipet bulb, 2 clamps, water and ethanol samples. Set up the viscometry apparatus as illustrated here.



REMEMBER: This apparatus is EXTREMELY fragile.

Carefully pour enough water into the right arm until the right bulb is full.

Place the pipet bulb over the right arm to JUST MAKE A SEAL and propel the water above point "X". After the water is above point "X" remove the pipet bulb. When the water reaches point "X", begin timing the flow of water to point "Y" and record this time in seconds in the data table below. Repeat this procedure until three trials have been performed, recording each time between points "X" and "Y" in the data table, below. Note that all you must do is record the time in the table -- the other values are already given to you in this table.

Data Table			
<u>η (H₂O)</u>	<u>10.08 millipoise</u>	<u>10.08 millipoise</u>	<u>10.08 millipoise</u>
<u>ρ (H₂O)</u>	<u>1 g/mL</u>	<u>1 g/mL</u>	<u>1 g/mL</u>
Δt (H ₂ O)	seconds	seconds	seconds

To calculate "C", substitute the values in EACH COLUMN into the following equation:

$$\frac{\eta_{\text{water}}}{\rho_{\text{water}} \Delta t_{\text{water}}} = C = \frac{10.08 \text{ millipoise}}{(1 \text{ g/mL})(\Delta t_{\text{water}})} = \frac{10.08}{\Delta t_{\text{water}}}$$

Place your calculated values of "C" in the spaces, below:

	Trial 1	Trial 2	Trial 3
C			

To determine the average calibration constant, "C", divide the sum of the above three values by three:

$$\text{Average } C = \frac{C_1 + C_2 + C_3}{3}$$

Your Average C (C Avg) = _____

Your average C, the calibration constant of your viscometer, is used for the next part of this experiment.

Obtain a sample of ethyl alcohol (EtOH) and determine its density (ρ_{EtOH}) as you did for water, in last week's experiment. Record your data, below:

Mass of 10 mL graduated cylinder and EtOH	g	g	g
Mass of 10 mL graduated cylinder	g	g	g
Mass of EtOH	g	g	g
Volume of EtOH	mL	mL	mL
(ρ_{EtOH})	g/mL	g/mL	g/mL
Average (ρ_{EtOH} Avg)			

You will need your average ρ_{EtOH} in the next portion of the experiment, as well.

Remove all of the water from your viscometer and blow air through the viscometer to "dry it out". After you are satisfied that it is as dry as possible, add EtOH to your viscometer and fill it as you did with your water. Repeat the procedure that you did with the water with your EtOH. Record and summarize your EtOH data in the table below. Multiply the first three values in each

column to determine the viscosity of the EtOH (4th row in each column) in your sample. Find the average viscosity, as well.

C Avg			
ρ_{EtOH} Avg			
Δt_{EtOH}			
η_{EtOH}			
η_{Avg}			

Questions

Complete the questions on this piece of paper. Attach this experiment with the others for turn-in.

The literature value for the viscosity of EtOH is in the table earlier in this write-up. How does it compare with your experimentally obtained value?

If the viscosity of a liquid is greater than the viscosity of water, does that mean the liquid is "sort of stickier" than water?