JOURNAL OF CHEMICAL EDUCATION

Laboratory Experiment

pubs.acs.org/jchemeduc

Introducing Students to Rheological Classification of Foods, Cosmetics, and Pharmaceutical Excipients Using Common Viscous Materials

Célia Faustino, Ana F. Bettencourt, António Alfaia, and Lídia Pinheiro*

Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Avenida Professor Gama Pinto, 1649-003 Lisboa, Portugal

Ⓢ *Supporting Information*

ABSTRACT: Rheological measurements are very important tools for the characterization of the flow and deformation of a material, as well as for optimization of the rheological parameters. The application and acceptance of pharmaceutical formulations, cosmetics, and foodstuffs depends upon their rheological characteristics, such as texture, consistency, or viscosity, which also influences their stability and bioavailability. This article describes a simple 2 h laboratory procedure for the rheological characterization of some foods, cosmetics, and pharmaceutical excipients using a digital Brookfield viscometer. The experiment was designed to introduce basic rheological concepts to undergraduate Health Science students, such as Pharmacy and Biochemistry students, allowing them to perform viscosity measurements of ideal and nonideal fluids and to classify the flow behavior based on the experimental flow curves of common viscous materials.

KEYWORDS: *First-Year Undergraduate/General, Laboratory Instruction, Hands-On Learning/Manipulatives, Consumer Chemistry, Drugs/Pharmaceuticals, Transport Properties*

Rheology studies the flow and deformation of matter.[1−6] Flow behavior is intrinsically associated with the viscosity of the fluid, a property that describes its resistance to flow under an applied stress. Viscosity arises from the friction between adjacent layers of fluid moving at different speeds. For laminar flow the velocity gradient is called the shear rate (SR), and the force per unit area creating or produced by the flow is the shear stress (SS). Typical SRs for some materials and processes are shown in Table 1.

Table 1. Typical Shear-Rate Ranges of Some Common Processes[3,4]

Process	SR range/s^{-1}	Applications
Sedimentation	10^{-6}–10^{-3}	Medicines, paints, spices in salad dressing
Extruding	10^{0}–10^{2}	Polymers, foods, soft solids
Pouring from a bottle	10^{1}–10^{2}	Foods, cosmetics, toiletries
Chewing and swallowing	10^{1}–10^{2}	Foods
Dip coating	10^{1}–10^{2}	Paints, confectionary
Mixing and stirring	10^{1}–10^{3}	Food processing, liquids manufacturing
Pumping (pipe flow)	10^{0}–10^{3}	Food processing, blood flow
Brushing	10^{3}–10^{4}	Brush painting, nail polish, lipstick
Spraying	10^{3}–10^{5}	Spray-drying, (fuel) atomization
Rubbing	10^{4}–10^{5}	Skin creams and lotions
Lubrication (engines)	10^{3}–10^{7}	Mineral oils, greases

The ratio of SS to SR corresponds to the viscosity of the fluid. SS is expressed in units of pressure (pascal, Pa) and SR in reciprocal time units (s^{-1}) so the viscosity SI unit is Pa s (1 Pa s = 1 kg m^{-1} s^{-1}). The cgs (centimeter-gram-second system) unit is the poise (1 P = 0.1 Pa s) although viscosity is commonly expressed in centipoises (1 cP = 0.01 P = 1 mPa s) as 1 cP is the viscosity of water at 20.2 °C.

In the simplest type of flow, SS (σ) is directly proportional to SR ($\dot{\gamma}$) and the proportionality constant is the viscosity (η) of the fluid, according to Newton's law for flow:[1−3]

$$\sigma = \eta\dot{\gamma} \quad (1)$$

Depending on the compliance to eq 1, fluids are classified as Newtonian or non-Newtonian. Newtonian fluids are characterized by a single viscosity value at constant temperature (Table 2), which is independent of both SR and duration of shear.

The viscosity of non-Newtonian fluids, i.e., the SS/SR ratio, changes when SR changes, thus being referred to as the apparent viscosity of the fluid.[1−3] This type of fluid can be classified as shear thinning or shear thickening if viscosity decreases or increases with increasing SR, respectively. A simple empirical relationship between SS and SR (eq 2, known as the power law model,[1−3,7−12] describes the behavior of this kind of fluid over a wide range of SRs:

DOI: 10.1021/ed4008364
J. Chem. Educ. XXXX, XXX, XXX−XXX

Table 2. Viscosities of Some Common Newtonian Fluids at 20 °C[3,4]

Fluid	η/cP
Air	0.018
Chloroform	0.58
Gasoline	0.7
Water	1.002
Ethanol	1.200
Mercury	1.554
Coffee cream	10
Olive oil	84
Castor oil	986
Glycerol	1490
Honey	10 000

$$\sigma = K(\dot{\gamma})^n \quad (2)$$

where K is the consistency factor and n is the flow behavior index, with $n < 1$ for shear-thinning fluids and $n > 1$ for shear-thickening fluids; for Newtonian fluids, $n = 1$ and $K = \eta$. In the limit of very low and very high SRs the viscosity of non-Newtonian fluids is constant and the two limiting values are called zero-shear (η_0) and infinite-shear (η_∞) viscosities, respectively. Typical values of n and K for common materials are shown in Table 3.

Table 3. Power Law Parameters (n, K) for Some Common Materials[3,4]

Material	n	K/Pa s^n
Fruit concentrate	0.7	2
Fabric conditioner	0.6	10
Polymer melt	0.6	10000
Molten chocolate	0.5	50
Synovial fluid	0.4	0.5
Apple puree	0.3	10
Sunblock lotion	0.3	75
Toothpaste	0.3	300
Tomato paste	0.2	70
Skin cream	0.1	250
Lubricating grease	0.1	1000

Rheological classification is based on the flow curve of the fluid, i.e., the plot of SS against SR (Figure 1). Newtonian fluids show a linear relationship between SS and SR, while shear thinning and shear thickening fluids exhibit negative and positive deviations, respectively. Flow curves that do not cross the origin are characteristic of plastic fluids, like ketchup, which require a minimum SS, called the yield stress (σ_0), to initiate flow. Typical yield stresses encountered for ketchup, mustard, and mayonnaise are around 15, 60, and 90 Pa, respectively.[3]

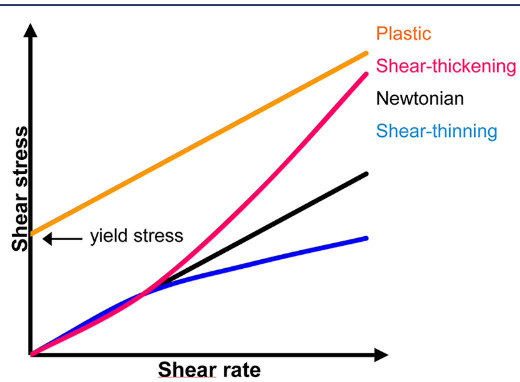

Figure 1. Flow curves for typical time-independent fluids.

The viscosity of non-Newtonian fluids, apart from being shear rate-dependent, may also be time-dependent. Thixotropy describes fluids whose viscosity decreases in time under a constant SR and recover their initial viscosity after removal of the applied stress.[13] The flow curve of a thixotropic fluid is characterized by a hysteresis loop, as the curves for increasing and decreasing SRs do not coincide. The rare, opposite behavior is called antithixotropy or negative thixotropy. Rheological classification of flow is summarized in Table 4.

Table 4. Rheological Classification of Non-Newtonian Fluids

Time-independent	Shear-thinning: viscosity decreases with increasing SR, e.g., blood, fruit juice concentrate, skin creams and lotions, shampoo.
	Shear-thickening: viscosity increases with SR, e.g., concentrated corn starch suspensions, sand/water mixtures.
	Plastic: exhibit a yield stress, e.g., ketchup, toothpaste, hand cream.
Time-dependent	Thixotropic: viscosity decreases in time, e.g., clay suspensions, blood, creams.
	Antithixotropic: viscosity increases in time, e.g., gypsum paste, concentrated latex dispersions.

Rheological analysis is a valuable tool in the food, pharmaceutical, and cosmetic industries, among others, being used for quality control of raw materials, intermediate products, final products, and manufacturing processes, such as mixing, pumping, packaging, and filling. The consumer acceptance of foodstuffs, pharmaceuticals, and cosmetics is also dependent on the flow properties of the final product, which are determinant for product performance, including bioavailability, formulation stability, and shelf-storage.[9−12]

The present laboratory experiment was designed to introduce basic rheological concepts to undergraduate Health Science students making use of foods, cosmetics, and pharmaceutical excipients encountered in everyday life. A digital Brookfield viscometer[14] is used, which can be replaced by the cheaper dial-reading version. This type of rotational viscometer measures the resistance offered by the fluid to the rotation of an immersed spindle, which is proportional to the viscosity of the fluid. Viscosity measurements obtained with Brookfield viscometers are relative values and depend on spindle geometry, rotational speed, temperature, measurement time, and sample volume.

The procedure is usually done in about 2 h by students working in pairs who select three fluids among the available set of nine. Students are encouraged to choose different fluids so that at the end of the lab session all fluids will have been analyzed and results compared. At the end of the lab session students are supposed to be able to perform rheological measurements using the Brookfield viscometer, classify rheological behavior, and calculate the rheological parameters from the experimental flow curves obtained.

EXPERIMENTAL PROCEDURE

Materials

Concentrated fruit juice, liquid yoghurt, solid yoghurt, shampoo, hair conditioner, glycerol 85% w/w, sodium carboxymethyl cellulose (CMC) 2% w/w, suspension of

DOI: 10.1021/ed4008364
J. Chem. Educ. XXXX, XXX, XXX−XXX

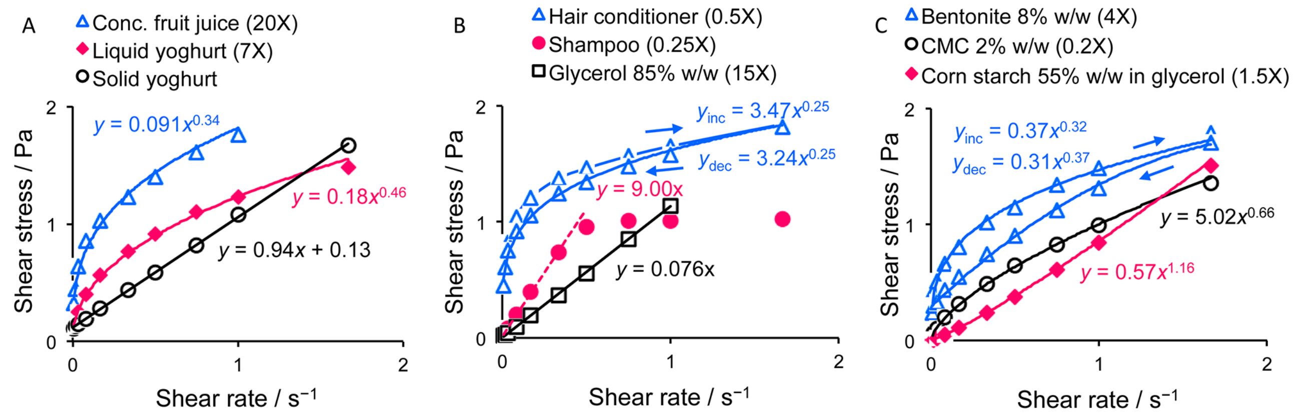

Figure 2. Typical flow curves for the foods (A), cosmetics (B), and pharmaceutical excipients (C) studied. The curves are fits to the power law model.

bentonite 8% w/w, and concentrated suspension of corn starch 55% w/w in glycerol.

Equipment

Digital Brookfield viscometer model LV DV-II+, with spindles LV1, LV2, LV3, and LV4.

Procedure

A 200 mL sample was poured in a 250 mL glass beaker with care to avoid the formation of air bubbles. The appropriate spindle was chosen based on the viscosity of the fluid, and viscosity measurements were taken at room temperature (25 °C), every 60 s, for ten selected SRs in the range 0.5−100 rpm (see Supporting Information). For each fluid, duplicate measurements were made, one at increasing SR and the other at decreasing SR, to account for time-dependent behavior. Experimental results were registered in the form of shear rate/viscosity tables created by the students in an Excel worksheet.

■ HAZARDS

All foodstuffs, cosmetics, and pharmaceutical excipients employed in the experiment are nonhazardous substances; however, the cosmetics used may be irritant when in contact with the eyes, and the pharmaceutical excipients, provided as solutions or suspensions to the students, are irritant to the skin and eyes. Students should thus wear protective clothing, gloves, and goggles and avoid contact of the samples with the eyes and skin.

■ RESULTS AND DISCUSSION

Representative flow curves obtained in a typical laboratory experiment are shown in Figure 2. The corresponding viscosity curves are provided in the Supporting Information.

From the experimental flow curves, students determined the power law parameters, K and n (data shown in Figure 2), by applying the power fit regression analysis option of the Excel worksheet, and commented on the values obtained.

Foodstuffs (Figure 2A)

Concentrated fruit juice and liquid yoghurt display shear-thinning behavior ($n < 1$), which has been reported in the literature for most fruit juice concentrates.[4] SR increase promotes the alignment of particles in the direction of shear, leading to a lower resistance to flow, therefore the viscosity of these fluids decreases with SR increase.

For solid yoghurt, the existence of a yield stress is due to the destruction of the yoghurt's structure necessary for flow to occur; once the yield stress is attained, SS increases linearly with SR, which is characteristic of ideal plastic behavior. By plotting SS against SR, a linear correlation is obtained, where the slope and the y-axis intercept correspond to the plastic viscosity (η_p = 0.94 Pa s) and the yield stress (σ_0 = 0.13 Pa), respectively.

Cosmetics (Figure 2B)

Glycerol is a Newtonian fluid often found in cosmetics and toiletries.[12] The viscosity for the aqueous solution of glycerol 85% w/w, corresponding to the slope of the SS versus SR linear plot, is 0.076 Pa s, in good agreement with literature values.[15,16]

For the hair shampoo tested, two distinct regions can be observed in the flow curve, as the sample behaves like a Newtonian fluid at low SR (<0.5 s^{-1}), displaying shear thinning behavior at higher SR. The zero-shear viscosity (η_0 = 9.00 Pa s) was determined from the slope of the linear region at low SR of the flow curve.

Hair conditioner showed shear-thinning thixotropic behavior that arises from the breakdown of the structure of the fluid, which is faster than its recovery at increasing SR. Hence, viscosities at decreasing SR are lower than the ones obtained at increasing SR and a hysteresis loop is present in the flow curve.

Pharmaceutical Excipients (Figure 2C)

Bentonite is used as medicinal clay and also as a suspending agent[12] in several pharmaceutical preparations. The flow curve for the studied suspension of bentonite shows a hysteresis loop characteristic of a thixotropic shear thinning fluid, whose viscosity decreases with time and also with increasing SR.

Sodium carboxymethylcellulose (CMC) or cellulose gum is an anionic water-soluble polymer commonly used as a thickening agent in pharmaceutical formulations.[12] CMC solutions show high viscosity even at low concentrations, and the studied CMC solution displayed time-independent shear-thinning behavior.

Corn starch is also used as a thickening agent,[12] and a suspension of corn starch 55% w/w in glycerol is a shear-thickening fluid ($n > 1$) where both viscosity and SS increase with SR. The viscous solvent prevents starch sedimentation and acts as a lubricant between the suspended particles but is squeezed out with increasing SR, leading to close packing of particles and increased friction.

DOI: 10.1021/ed4008364
J. Chem. Educ. XXXX, XXX, XXX−XXX

CONCLUSION

This simple and nonhazardous laboratory experiment allows the rheological characterization of pharmaceutical excipients, cosmetics, and foodstuffs making use of an easy-to-operate digital Brookfield viscometer. The experiment offers a wide range of samples relevant to the pharmaceutical, cosmetic, and food industries and the flexibility to be directed only to one type of sample, according to course preferences or time constraints. Students get acquainted with viscosity concept and measurement and also with nonideal fluid behavior based on viscous materials found in everyday life.

ASSOCIATED CONTENT

Supporting Information

A student handout, instructor notes, including CAS registry numbers for all chemicals, safety warnings, and experimental flow curves. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lpinheiro@ff.ul.pt.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors dedicate this paper to Professor Joaquim Cotta do Amaral, former Professor responsible for the Physics course at FFUL and now retired.

REFERENCES

(1) Goodwin, J. W.; Hughes, R. W. *Rheology for Chemists: An Introduction*; The Royal Society of Chemistry: Cambridge, 2008.

(2) Blair, S. *Elementary Rheology*; Academic Press: London, 1990.

(3) Barnes, H.; Hutton, J.; Waters, K. *An Introduction to Rheology*; Elsevier: Amsterdam, 1989.

(4) Steffe, J. F. *Rheological Methods in Food Processing Engineering*, 2nd ed.; Freeman Press: East Lansing, 1996.

(5) Bermudez, V. Z.; Almeida, P. P.; Seita, J. F. How to learn and have fun with poly(vinyl alcohol) and white glue. *J. Chem. Educ.* **1998**, *75*, 1410−1418.

(6) Doraiswamy, D. The origins of rheology: A short historical excursion. *Rheol. Bull.* **2002**, *71*, 7.

(7) Perrin, J. E.; Martin, G. C. The viscosity of polymeric fluids. *J. Chem. Educ.* **1983**, *60*, 516−518.

(8) Wilkes, G. L. An overview of the basic rheological behavior of polymer fluids with an emphasis on polymer melts. *J. Chem. Educ.* **1981**, *58*, 880−892.

(9) Briceño, M. I. Rheology of Suspensions and Emulsions. In *Pharmaceutical Emulsions and Suspensions*; Nielloud, F., Marti-Mestres, G., Eds.; Marcel Dekker: New York, 2000; Vol. *105*, p 557.

(10) Barnes, H. A. Rheology of emulsions—a review. *Colloids Surf., A* **1994**, *91*, 89−95.

(11) Motyka, A. L. An introduction to rheology with an emphasis on application to dispersions. *J. Chem. Educ.* **1996**, *73*, 374−380.

(12) Tadros, T. F. *Rheology of Dispersions—Principles and Applications*; Wiley-VCH: Weinheim, 2010.

(13) Barnes, H. A. Thixotropy—a review. *J. Non-Newtonian Fluid Mech.* **1997**, *70*, 1−33.

(14) Brookfield Engineering Laboratories. http://www.brookfieldengineering.com/products/viscometers/index.asp (accessed Sep 2013).

(15) Cheng, N. S. Formula for viscosity of glycerol-water mixture. *Ind. Eng. Chem. Res.* **2008**, *47*, 3285−3288.

(16) Segur, J. B.; Oberstar, H. E. Viscosity of glycerol and its aqueous solutions. *Ind. Eng. Chem.* **1951**, *43*, 2117−2120.

DOI: 10.1021/ed4008364
J. Chem. Educ. XXXX, XXX, XXX−XXX