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EXERCISE 10

Flow behavior of polymer solutions

Fundamental notions: viscosity, shaear stress, shear rate, non-newtonian fluids

Introduction

Viscosity is a measure of a fluid's resistance to flow and it can be considered as the internal friction resulting when a layer of fluid is caused to move in relation to another layer. If two parallel layers of fluid of area *A,* separated by a distance *dx,* are caused to move at different velocities v_1 and v_2 (v_1-v_2=dv) by a tangential force *F* (see Fig.1), the viscosity η is defined as:

$$\eta = \frac{\frac{F}{A}}{\frac{dv}{dx}} \qquad (1)$$

where dv/dx is the velocity gradient perpendicular to the direction of flow. This velocity gradient is called the shear rate, whereas the force per unit area, F/A, is called the shear stress.

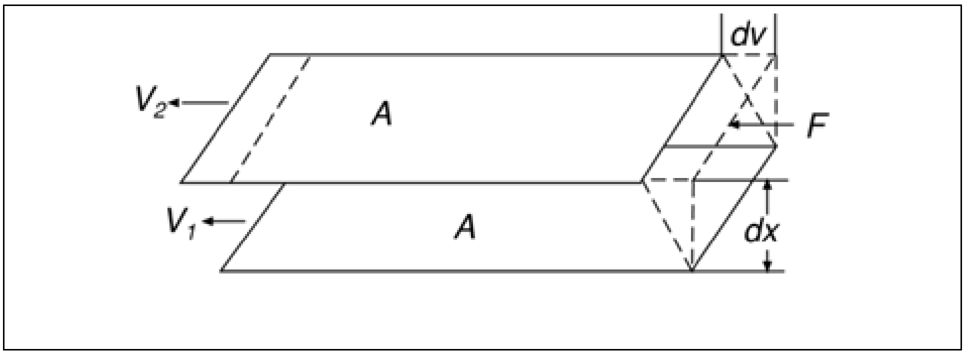

Fig. 1. Definition of viscosity (see the text)

Thus, the viscosity can be expressed in terms of shear stress, τ, and shear rate, γ :

$$\eta = \frac{\tau}{\gamma} \tag{2}$$

Fluids can be classified into two categories: Newtonian and non-Newtonian. Newtonian fluids are those having, at a given temperature, a constant viscosity, independent of the applied shear stress (or the shear rate). Fluids which cannot be defined by a single viscosity value at a specified temperature are referred to as non-Newtonian. Apart from being shear stress (or shear rate) dependent, the viscosity of non-Newtonian fluids may also be time dependent, in which case the viscosity is a function not only of the duration, but - in most cases - also of the frequency of successive application of shear. In the case of non-Newtonian fluids the term “apparent viscosity”, defined as the ratio of shear stress to shear rate at a given shear stress or shear rate, is used.

The flow behavior of non-Newtonian time independent fluids may be classified as specified in Tables 1 (compare also Fig.2).

Table 1. The major types of fluid flow behavior.

Shear thinning (or **pseudoplastic**)	**Shear thickening** (or **dilatant)**	**Viscoplastic**	
		Bingham	**Casson**
apparent viscosity reduces as the shear rate increases	apparent viscosity increases as the shear rate increases	fluids behave Newtonian when a threshold shear (yield value) is exceeded (fluids do not flow until the yield stress is reached)	yield stress must be reached before any velocity gradient can occur (like in the case of Bingham fluids), but the relation between stress and the rate of deformation is not linear
E.g. paints, shampoo, ketchup	E.g. wet sand, concentrated starch suspensions	E.g. tooth paste, hand cream,	

Depending on how the viscosity changes with time the flow behavior is characterized as specified in Table 2:

Table 2. Types of time-dependent fluid flow.

Thixotropic	**Rheopectic** (or **antithixotropic)***
time thinning (apparent viscosity decreases the longer the stress is applied)[1]	time thickening (apparent viscosity increases the longer the stress is applied)
common in food and chemical industry (e.g. yoghurt, paint)	very rare (e.g. gypsum paste)

*sometimes these terms are distinguished[2]

The above classification is arbitrary – the real system often exhibit two or even more types of non-Newtonian behavior.

Non-Newtonian behavior reflects the complexity of the internal structure of a fluid. This behavior is commonly observed in soft matter systems, which are sometimes referred to as “structured liquids”, and whose properties are governed by weak interactions (that is interactions whose energy scale is comparable to that of thermal energy) between the constituents. Flow perturbs the interactions and – as a result – a complex molecular or nanoscale structure. Shear thinning behavior is more common than shear-thickening. For instance, it can be originated from the breakdown of the molecular network structure or from the disorientation or disentanglement of macromolecules under shear (the last case will be discussed in detail later). The opposite, less-common, shear-thickening behavior can be attributed, for instance, to the conversion of intramolecular to intermolecular interactions in polymer solutions or the aggregation due to shear

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[1] If decrease in η (apparent) is irreversible the behavior is often called shear-break-down.

[2] **Anti-thixotropy** (called also as negative thixotropy) - build-up of an otherwise non-existent structure occurs under shear. Structure disappears with removal of shearing. Thus negative thixotropy refers to an increase in viscosity with time only during shearing, and this increase is completely reversible [3].
Rheopexy – materials showing rheopexy break down during (strong enough) shearing, but their rebuild is faster at very low shear rates than at complete rest (thixotropic materials will regain their structure faster at rest than at low shearing rates). Thus rheopexy deals only with an acceleration of a reconstruction that should take place without the shearing, albeit slower.

induced bond formation in concentrated suspensions (e.g., the shear induced flocculation). This could also result from the jamming of high aspect ratio particles due to rotation by the shear flow.

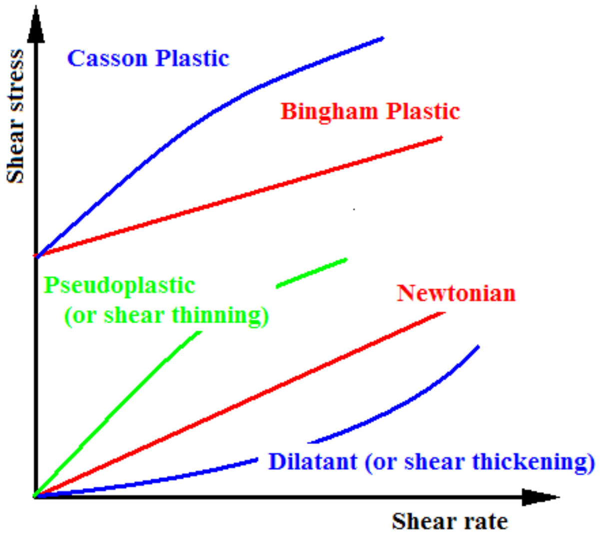

Fig.2. Classification of non-Newtonian time independent fluids

In most fluids which display a shear-dependent behavior, the dependence of the viscosity on the duration and history of shearing is also observed. Deformation destroys the inherent structure of structured liquid and the structure recovery requires time, resulting in thixotropic/anti-thixotropic effects. There are also cases where the breaking down of bonds is irreversible, such as polymer gels. Here, the viscosity will not recover after the stress has been removed. There are still other cases, such as liquid crystals, where the structures do not break down irreversibly, but the recovery time is long compared to any processing time scale. In this case, also there will not be any recovery on the time scale of observation, and the change in structure will appear irreversible.

Several models are available for mathematical description of the flow behavior of non-Newtonian fluids. These models relate the shear stress of a fluid to the shear rate. One of the most widely used models is the "Ostwald de Weale" model or the power law model, described by the equation (3):

$$\tau = \kappa \gamma^{n} \tag{3}$$

where κ and n are empirical parameters dependent on the properties of the fluid and the temperature. The constant κ is a measure of the consistency of the fluid:

the higher the κ is, the more viscous the fluid is. The exponent n (often referred as the flow behavior index) is a measure of the degree of non-Newtonian behavior: the greater the departure from the unity, the more pronounced the non-Newtonian properties of the fluid are. The apparent viscosity for the power-law fluid can be expressed as:

$$\eta = \kappa \, \gamma^{n-1} \tag{4}$$

For a shear thinning fluid $n < 1$, whereas $n > 1$ for a shear-thickening one. When $n = 1$, eq (4) reduces to the case of a Newtonian fluid.

One of the disadvantages of the power-law model is that it fails to describe the viscosity of many non-Newtonian fluids (e.g., suspensions or polymer solutions) in very low and very high shear rate (or stress) regions (the viscosity is constant – but at different levels - in the limit of low and high values of shear rate/stress). Equations that predict such a shape of the rheological curve require at least four parameters. One such is the Cross equation:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + K \, \gamma^n} \tag{5}$$

where η_0 and η_∞ refer to the asymptotic values of viscosity at very low and very high shear rates, respectively, K and n are two other model parameters. In the intermediate region, where $\eta \ll \eta_0$ and $\eta \gg \eta_\infty$ the equation (5) simplifies to the "power law" form.

One of the simplest viscoplastic models is the Bingham plastic model. The ideal Bingham material is an elastic solid at low shear stress values and Newtonian fluid above a critical value called the Bingham yield stress. The relationship between shear stress and shear rate is of the form:

$$\tau = \kappa_\mathrm{B} \, \gamma + \tau_\mathrm{y} \ \text{ when } \tau \geq \tau_\mathrm{y} \ \text{ and } \gamma = 0 \ \text{ when } \tau \leq \tau_\mathrm{y} \tag{6}$$

where κ_B and τ_y are constants interpreted as the plastic viscosity and the yield stress, respectively. However, the Bingham plastic model does not have the ability to handle the shear-thinning characteristics of non-Newtonian fluids. The Casson model accounts for both the yield stress and the shear-thinning behavior:

$$\sqrt{\tau} = \kappa_\mathrm{C} \sqrt{\gamma} + \sqrt{\tau_\mathrm{y}} \ \text{ when } \tau \geq \tau_\mathrm{y} \ \text{ and } \gamma = 0 \ \text{ when } \tau \leq \tau_\mathrm{y} \ \ \tau \leq \tau_\mathrm{y} \tag{7}$$

where κ_C is a model constant.

The Herschel-Bulkley model, also called the generalized power law equation, extends the simple power-law model to incorporate both the yield stress and pseudoplasticity as follows:

$$\tau = \kappa \, \gamma^n + \tau_\mathrm{y} \ \text{ when } \tau \geq \tau_\mathrm{y} \ \text{ and } \gamma = 0 \ \text{ when } \tau \leq \tau_\mathrm{y} \tag{8}$$

where κ and n are model constants. The main benefit of the generalized power law equation is its applicability to a great number of non-Newtonian fluids over a wide range of shear rates.

There are a number of different methods and techniques for measuring the viscosity of fluids and many different types of commercial instruments (viscometers and rheometers[3]) are available. Rheological measurements are often performed in rotational rheometers in which the test material is deformed between two coaxial cylinders, cones, plates, or cone and a plate. Most instruments are based on the rotation relative to the common central axis. Measuring devices with the coaxial cylinder system can be divided into two main categories, depending on whether the inner or outer cylinder rotates, known as Searle and Couette system, respectively. Rotational instruments may be operated in steady shear (constant angular velocity) or oscillatory (dynamic) mode. Some instruments function in the controlled stress mode, the other – in the controlled rate.

Polymer additives are used extensively to modify the rheological properties of solutions in a wide variety of industrial applications (e.g. in food industry and pharmaceutics as thickeners, binding agents or wetting agents; in pills production, in lubricants for viscosity index improvement of motor oils; in petroleum industry to decrease resistance of viscous flow; in water handling facilities for waste water treatment, and in many other fields). One of the most widely used polymers is polyacrylamide (PAAm), a synthetic, water soluble polymer derived from acrylamide monomer. PAAm is extensively used in such fields as soil conditioning, paper pulp processing, waste water treatment and mineral processing. One of the important applications of PAAm is in enhanced oil recovery where aqueous PAAm solutions of high viscosity are pumped into an oil wells. The average molecular mass of commercial PAAm ranges approximately from $1 \cdot 10^3$ to $15 \cdot 10^6$ D.

The way polymer containing liquids flow differs significantly from the behavior of simple liquids. In solution, macromolecules can assume a variety of shapes, depending on the nature of the chain and their interaction with the solvent. These differences are reflected in the viscosity and other rheological properties. In response to a deformation the polymer molecule itself can change both its shape and orientation.

For the sake of illustration, let us consider the flow behavior of solutions of a linear homopolymer, like PAAm. In good solvents, polymer chains swell and take on coiled shapes. In the absence of flow the individual coils assume an equilibrium conformation. Upon shearing, the solvent may flow through coils,

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[3] A rheometer is used for those fluids which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer

whereby each polymer segment may experience a frictional drag causing a disturbance of conformation of the coils. The chains will try to rearrange themselves by diffusion to regain their equilibrium conformation. At low deformation rates Brownian motion is strong enough to offset the viscous pull of solvent (or, in other words, the relaxation time is small compared to the reciprocal of the rate of deformation and the system has sufficient time to relax to its equilibrium state within the deformation time scale) and the viscosity of the solution remains constant. With increasing shear rate the time scale of deformation becomes shorter than that of the relaxation time, implying that macromolecules no longer deform fully during a rotation, leading to lower energy dissipation and consequently to a lower viscosity. As deformation rates continue to increase, the coils can uncoil into strings completely aligned with the flow. As a result, above a certain value of shear rate the viscosity of dilute polymer solution remains constant (i.e., it does not change with the increasing shear rate).

The above described effect of shear on the conformation and dynamics of polymer molecules is valid only for the dilute solutions, whose rheology is dependent solely on the dynamics of individual chains and the number of chains (i.e. the concentration) in the system. In dilute polymer solutions the shear-thinning effect is weak.

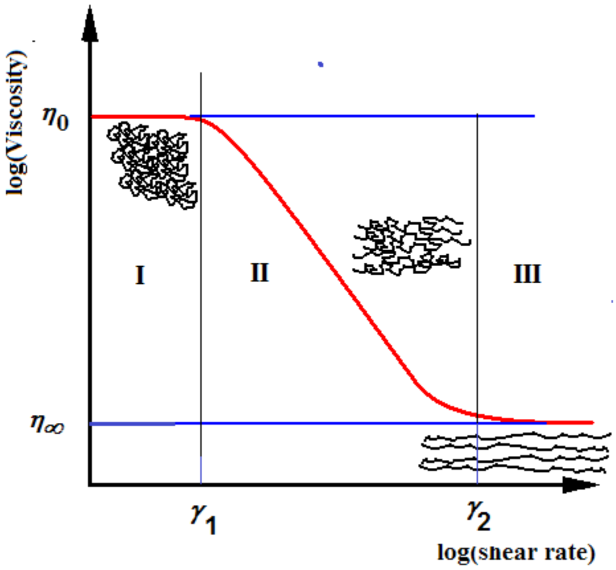

Fig. 3. The flow curve for a polymer solution showing the two regions of complete entanglement and complete alignment.

In concentrated solutions of linear polymers the polymer coils are extensively entangled with each other (for illustration see Fig. 3). Entanglements will restrict the motion of the polymer, and therefore increase the relaxation time. For flow to occur, entanglements have to disentangle. This cost a relatively large amount of energy dissipation which is measured macroscopically as a high viscosity. As the number of entanglements increases strongly with polymer concentration, and at constant mass concentration with the polymer dimensions, this explains qualitatively the strong dependence of viscosity on concentration and the molecular mass. At low shear rates and steady state conditions, as many entanglements will be formed by Brownian motion as are disentangled, per unit time, and thus the system behaves like Newtonian fluids (first Newtonian plateau, Fig. 2). With increasing shear rates the extent of disentangling increases, and above a certain shear rate this can no longer be compensated by entanglement formation. A new steady state develops in which the number of entanglements between the polymer molecules is lower. This implies that, for further shearing to occur, fewer entanglements have to be loosened, resulting in lower energy dissipation and so in a lower apparent viscosity. At high shear rates the time available for formation of entanglements becomes too short and when the shear rate reaches or exceeds a certain value the polymer molecules remain fully disentangled. Then the viscosity becomes constant again and this region is referred to as the second Newtonian plateau (Fig. 2). As the relaxation time decreases with the viscosity and also does so with the polymer concentration, the lowest value of shear rate at which the second plateau occurs will increase with decreasing polymer concentration.

If the disentangling and reformation of entanglements take some time, the thixotropic behavior of concentrated polymer solution can be observed.

Experimental

The goal of the experiment is to investigate the flow behavior of PAAm solutions of different concentrations. To this end the dependencies between the solution viscosity and the shear rate should be determined. An investigation of a possible dependence of the solution viscosity on the time of shear at, at least, two different shear rates should be performed[4].

Materials and apparatus

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[4] One should be aware that the viscosity of a thixotropic fluid is a function not only of the shearing stress, but also of the previous history of motion within the fluid.

- PAAm (Aldrich, molecular mass $5 \cdot 10^6$) dissolved in 50/50mixture by mass of water and glycerol in the concentration range between 0,1 -2,5% (Because in the case of very-high-polymers the dissolution rate is very low, the PAAm solutions should be prepared at least 2 weeks in advance.)
- Rotational viscometer produced by Fungilab S.A., model Expert L PPR(The description of the instrument and operation manual, given by the producer, are available at the website of this course) equipped with a small sample adapter APM/B. The adapter, thanks to its known cylindrical geometry shape, allows to get shear rate and shear stress determinations. Only a small quantity of a sample is needed.

Measurement of apparent viscosity and shear stress

I. Assembly of the small volume adapter

The small sample adapter consists of a cylindrical sample chamber container, mounting channel, two mounting screws, bottom stopper with the temperature sensor, upper stopper, hook and thread and 3 coaxial spindles (TL5, TL6, TL7). The manufacturer offers two types of such adapters: with and without the circulation jacket. The adapter APM/B without the circulation jacket, which is used in the experiment, allows the user to control the temperature by immersing the accessory chamber in a thermostatic bath (as shown in Fig.4).

Fig. 4. Left picture: Assembled APM/B small volume adapter. Right picture: APM/B immersed in a thermostatic bath.

Assemble the small volume adapter according to instructions given below (see also Fig.5 which explains the assembly of the APM/B adapter and its connection to the viscometer):

- Check if the digital viscometer is correctly fastened to the base.
- Fasten the mounting channel to the hole at the back of the viscometer metallic vase.
- Fasten the sample chamber container to the mounting channel.
- Connect the temperature sensor of the sample chamber container with the viscometer (the socket is in the back of the viscometer).
- Fill the outer cylinder with appropriate volume of the polymer solution (as specified in Table 3) using the automatic pipette. Take care not to introduce air bubbles during this process.
- Insert the spindle into the solution. IMPORTANT: Do this slowly since the spindle must be inserted correctly in the sample. When working with a more viscous sample be careful to avoid pulling the spindle upwards. Hold the spindle connector.
- Connect the hook with the spindle.
- The other end of the hook connect with the viscometer. The viscometer incorporates the PPR system (Push, Plug and Play). You should attach the spindle using the following three steps (compare also Fig.6):

  Step 1: Select your spindle for coupling to your unit and push the main axis.

  Step 2: Plug the spindle while subjecting the main axis.

  Step 3: Release the main axis and the spindle will be completely coupled.
- Check the level of the sample. It should be approximately in the middle of the cone, which is connected to the hook. Figure 7 shows more information about this.
- Place the upper stopper over the sample container.
- Detach the spindle before running the autotest (see sec.II. Measurement).

Table 3. Spindles features and sample volumes dependent on the type of the spindle used.

Spindle	Shear rate [s^{-1}] *)	Sample volume [ml]
TL5	1,32 x RPM	8,0
TL6	0,34 x RPM	10,0
TL7	0,28 x RPM	11,5

*) Shear rate is calculated based on the features of Newtonian liquids.

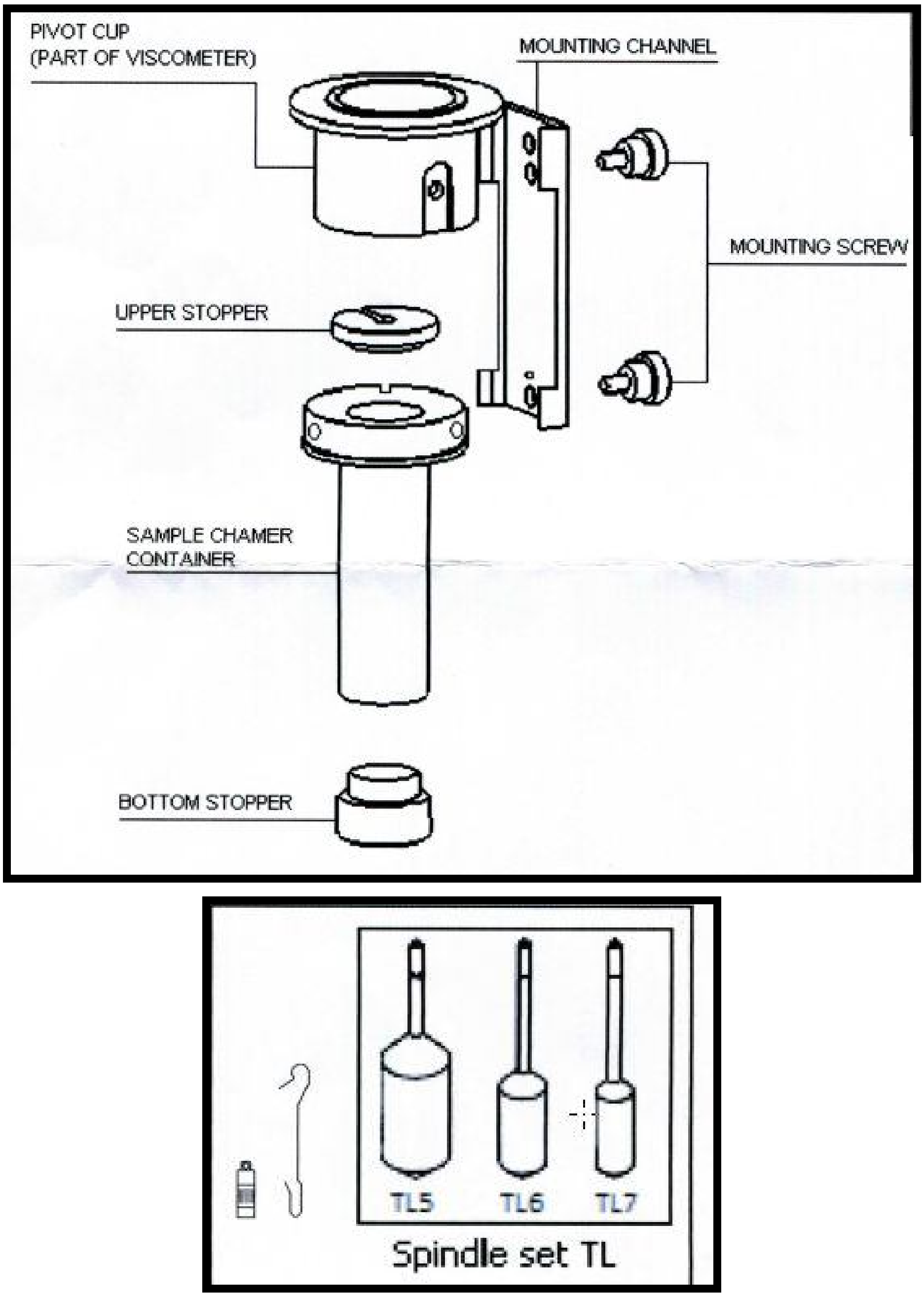


Fig. 5.: Parts of the small volume adapter APM/B

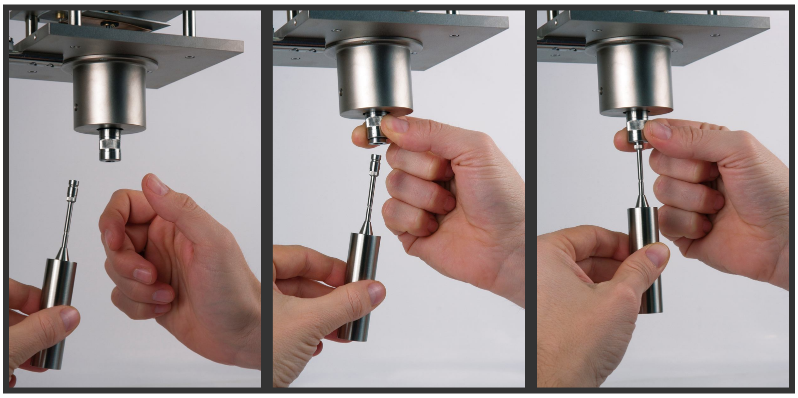


Fig. 6. Illustration of the spindle attachment with the PPR system.

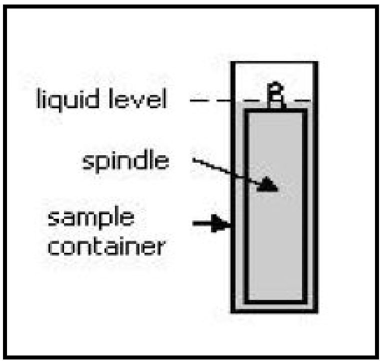


Fig.7. Correctly filled the small volume adapter.

○ In order to replace the spindle or the sample remove the old spindle by detaching the hook from the viscometer and lower the spindle slowly into the sample container. Next, disconnect the sample container and remove the spindle carefully. Wash both the spindle and the sample container with warm water and next dry them using the filter paper (or the paper towel).

II. Measurement

- Level the viscometer referring to the bubble level on the instrument (to do this use the adjustment screws of the support base).

- Verify that the power cable is connected to the equipment and that the power cable is connected to the power. Also check the connection between the instrument and the computer.

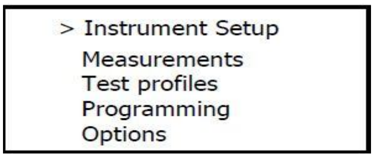
- Turn on the switch on the back of the machine. The machine will beep, indicating that it has started and it will show the following screen:

```
FUNGILAB S.A
V.1.0
EXPERT SERIES
English
```

- Run the autotest. The Test-run menu allows you to verify the operation of the viscometer in a way that allows detection of motor malfunctions in a simple and practical way. The following message will appear on the screen:

```
AUTOTEST
Remove the
Spindle and
press <ENTER>
```

VERY IMPORTANT: The Test-run should be carried out without a spindle. In the case of a successful check, the machine will beep once it is finished and the following main menu will appear:

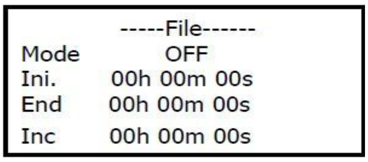


```
> Instrument Setup
  Measurements
  Test profiles
  Programming
  Options
```

- Attach again the spindle to the viscometer.

- From the main menu screen, with the '►' cursor over the 'Options' field, press the 'ENTER' key twice to choose this option.

- If you choose the output option you will be activating experiment recording. For this, you will be led to the following screen:



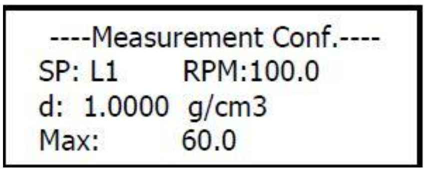
```
        -----File------
Mode          OFF
Ini.     00h 00m 00s
End      00h 00m 00s
Inc      00h 00m 00s
```

The default mode is 'OFF'. To activate this option, use the '▲' or '▼' to turn it 'ON'. Once the field is active, you can select different fields, jumping for one to another using the '►'key. To modify each field, hit 'ENTER'. The selected field will blink on the screen until it is modified, using the numerical keypad and introducing the desired values in the digital places this way. Upon digit entry the viscometer will automatically jump to the next digit place. To save the changes hit 'ENTER', which will unselected the field and save the values entered. (Note: The exit keys 'MEM/CLEAR' and the '◄' key will bring you to the main menu screens or the previous screen, respectively. With the 'MEM/CLEAR' key, the changes will go unsaved.

- Ini: record start time, 'Beginning' (e.g. 00:00:00)
- End: data record end time. (e.g. 05:00:00)
- Inc: the increments by which samples are taken (the appropriate setting will depend mainly on the selected rpm value).

For the proper selections of settings consult your instructor.

- Next, from the main menu screen you can begin the configuration of the measurement. When you choose the field 'Measurement' and next press 'ENTER' you will be brought to a screen resembling this one:



----Measurement Conf.----
SP: L1 RPM:100.0
d: 1.0000 g/cm3
Max: 60.0

To move through the fields cyclically use the '►' key and with the 'ENTER' '▲' and '▼' keys you can proceed to edit each one of the fields. Let's first look at what each field represents and how to modify it.

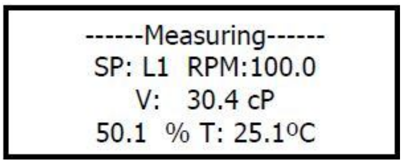
- SP: the field that indicates which spindle we use for the measurement.
- RPM: the field indicating the working speed.
- d: indicates the density of the sample
- Max: Maximum viscosity to be determined with the speed and the spindle selected.

The SP field together with the selected speed will determine the maximum and minimum viscosity values, as well as the existence of a shear stress measurement (if you're using coaxial spindles). To modify the spindle, you first need to select the field using the 'ENTER' key. The viscometer will only show the spindles that are compatible with your model. **By pressing 'ENTER' and the '2 M2' key you select the TL-group spindles.**

The RPM field (revolutions per minute) indicates the speed at which the test will be done. The EXPERT series incorporates 54 pre-determined speeds: 0.01, 0.03, 0.05, 0.07, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.4, 1.5, 1.8, 2, 2.5, 3, 4, 5, 6, 7.5, 8, 10, 12, 15, 17, 20, 22, 25, 30, 35, 40, 45, 50, 60, 70, 75, 80, 90, 100, 105, 120, 135, 140, 150, 160, 180, 200 RPM. The viscosity of the liquid and the spindle used determine the speed (refer to tables 8 to 18 of the instruction manual). Speed modification: once the corresponding field is selected using the '►' key, you can move through the pre-established speed using the '▲' and '▼' keys. If you want to keep the selected speed, press the '►' key to change parameters.

<u>The 'd' (density) field</u>: Indicate the density of the fluid being measured. NOTE: If you modify the density, the viscometer will give its measurements in cSt (centiStokes), whereas if you conserve the initial density (considered the density by default), the measurements will be in cP (centipoises), P (Poise) or mPa·s, Pa·s.

- By pressing the 'ON' key after the introduction of the measurement parameters the viscometer will start moving the spindle, which means that the equipment is ready to start collecting data. NOTE: If, once the values of all of the fields are confirmed, you press the 'MEM/CLEAR' key (instead the "ON" key), you'll return to the main menu screen, losing all of the data introduced in measurement configuration. If you press the '◄' key, you will also lose the values entered, returning to the initial screen.). When pressing the 'ON' key you can access the screen similar to the following:



```
------Measuring------
SP: L1  RPM:100.0
V:   30.4 cP
50.1  % T: 25.1ºC
```

As the equipment goes about collecting viscosity data (one piece of data for each rotation of the spindle), the information on the screen will be updated. On the screen you will see:

- SP: Current spindle (selected on the previous screen).
- RPM: Revolutions per minute. Value selected on previous screen.
- d: Viscosity. Value expressed in cP or mPa·s, or cSt (in the case that a density different from the default one is introduced).
- %: Certain percentage of the base scale. Percentage value of the curvature of the spring in relation to the base of the same scale.
- T: Temperature of the sample (ºC or ºF).

NOTE: The speed field will be blinking until the motor speed is stable.

NOTE: Depending on the selected speed, it is possible that the speed reading will take a few seconds or minutes to appear. It's important that the viscometer has made at least five rotations (which equals five measurements) before considering the measurements to be valid, as the device needs that time to stabilize. It’s also important to only take into account the temperature of a stable sample.

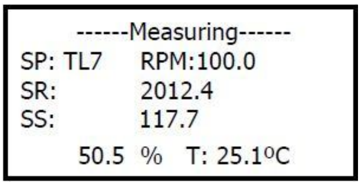
In addition to visualizing measurements made on the sample, the user can also do other things from this screen.

Using the ‘▲’ and ‘▼’ keys, you can increase or reduce the speed of the spindle’s rotation (RPM). When you hit one of these two keys, the rotation speed increases or decreases, respectively, from the previous speed. In this way, we can comfortably modify the turning speed without having to leave the measurement screen. When you make a speed change, the field will start blinking again until the motor speed stabilizes.

IMPORTANT: When the certain percentage of the base scale is lower than 15% or is as high as 100%, the measurement cannot be considered valid and the equipment will emit a warning beep with every rotation made under these circumstances.

With the ‘ON’ key you can stop or start the motor, which allows for momentary pauses in an experiment. If you next press the ‘MEM/CLEAR’ key, the viscometer will abandon the measuring and return to the main screen, while if you hit the ‘ON’ key again, the equipment will restart the measurements with the same configuration.

- Shear rate and shear stress determinations: By pressing ‘ENTER’ in the main measurement screen, the following screen will appear:



```
      ------Measuring------
SP: TL7     RPM:100.0
SR:         2012.4
SS:         117.7
      50.5  %   T: 25.1ºC
```

By pressing the ‘ON’ key from this screen, we stop the motor, and by pressing it again, the measurements start back up (in the same way as previously described). The fields we can see here are:

- SP: Selected spindle.
- RPM: Spindle speed in revolutions per minute.
- SR: Shear Rate
- SS: Shear Stress.
- %: Certain percentage of the base scale. Percentage value of the curvature of the spring in relation to the base of the same scale.
- T: Temperature of the sample (ºC or ºF).

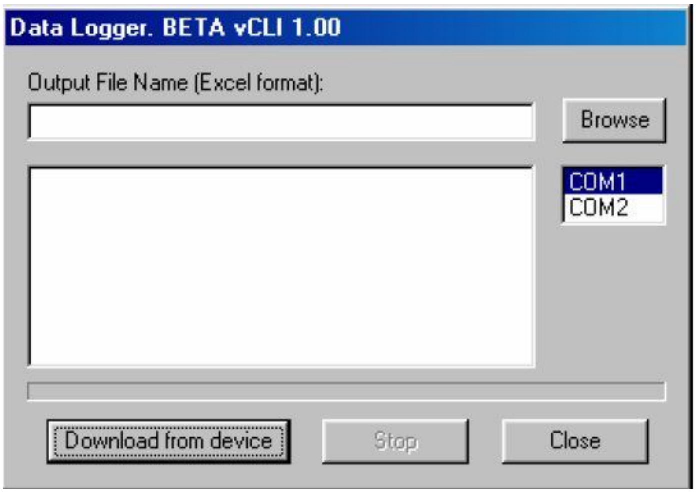
It is not necessary to always return to the main measurement screen. The keys ‘ENTER’, ‘5M5’ and ‘◄’ all allow you to return to the previously described screens.

III. Data transfer from the viscometer to the PC

The Datalogger application allows the transfer of data from the stored file in the viscometer to the PC, assuming that the latter disposes of the adequate input/output configuration. When the data is received, the program will generate a Microsoft Excel-compatible file containing the received data.

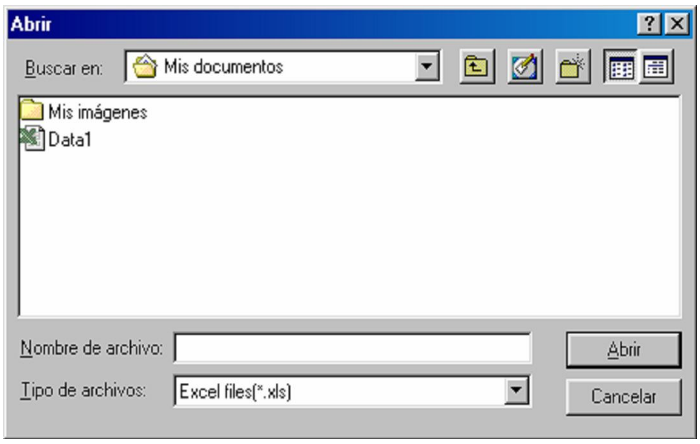
IMPORTANT: In order to successfully transfer the data from the viscometer to the computer you should stop the spindle rotation and go the main menu screen using the ◄ key. Transfer the data after each modification of the measurement parameters.

At the start of the program, you will see the following window:



In the first screenshot you can see different controls and edition lines. Starting from top to bottom, you can see an edition line where you should edit the name of the file where the data from the viscometer will be saved. It will be necessary to introduce the complete path for the file, which should have the extension *.xls.

If you want to see the standard window for file selection, click the ‘Browse‘ bottom. If you select the name of the file through this window, the extension *.xls will be added automatically.

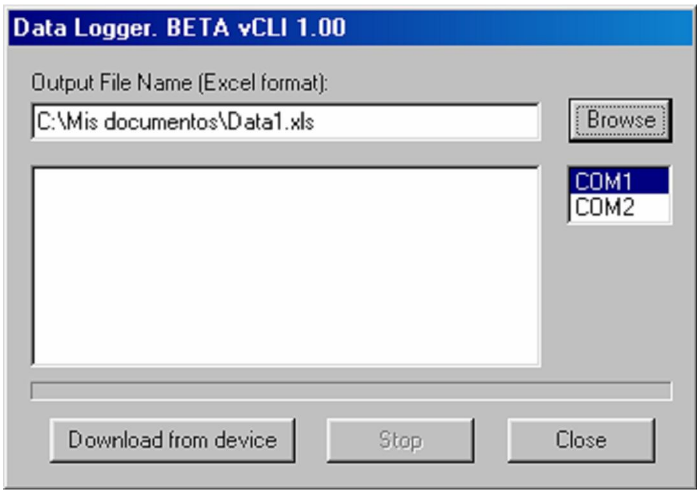


Buscar en: Mis documentos

Nombre de archivo:

Tipo de archivos: Excel files(*.xls)

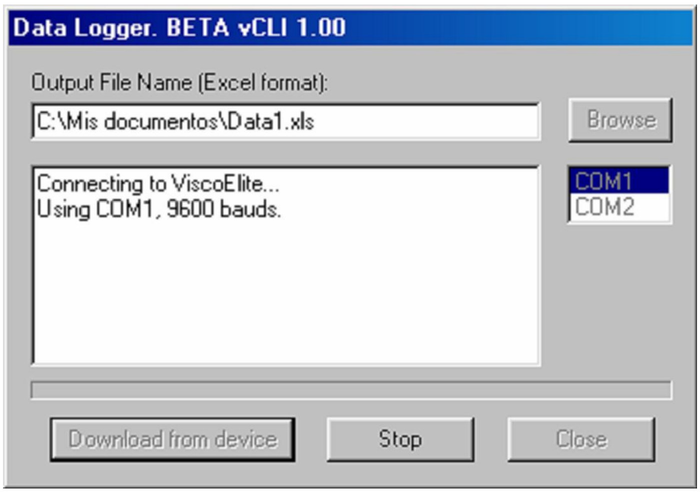
Once the file with the data that you wish to use is selected, you will have to choose the communication port through which you will make the connection.



Output File Name (Excel format): C:\Mis documentos\Data1.xls

Once the port series you wish to use is selected, you can proceed to download the information from the viscometer. To execute this download you will have to press the 'Download from device' bottom. Upon doing this for the first time you will see that the majority of commands in the main window will be deactivated ('Browse', 'Close' and even 'Download from device'), while the 'Stop' command will become active and information messages about the progress of the importation process will appear.

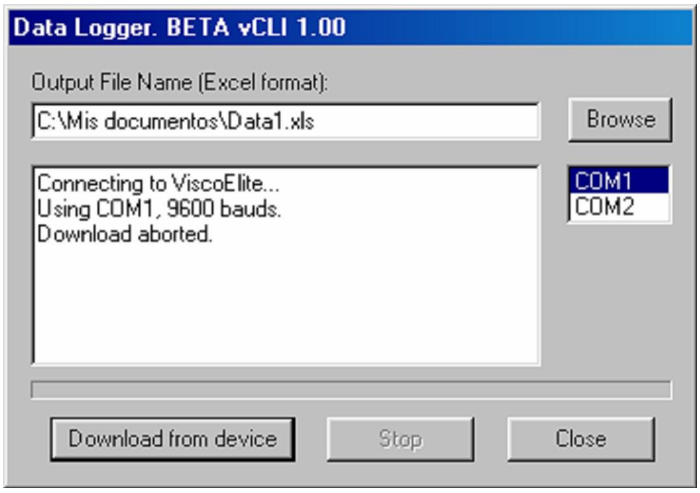
The first messages are about the connection status, as you can observe in the following screenshot. The program will indicate the port and the connection speed used with the equipment.



C:\Mis documentos\Data1.xls

```
Connecting to ViscoElite...
Using COM1, 9600 bauds.
```

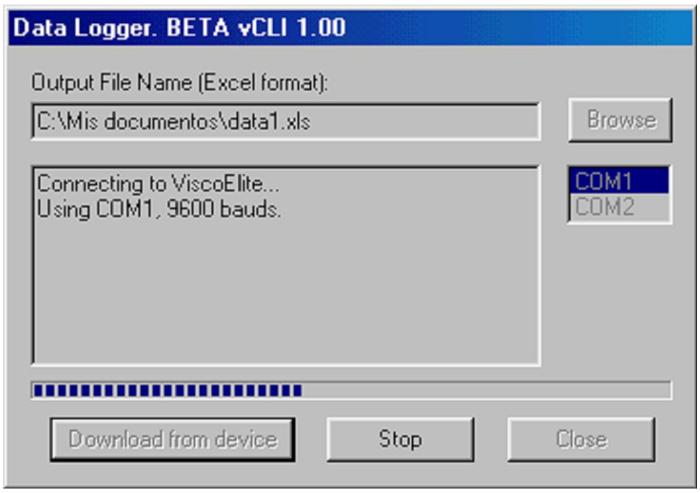
If the user sees that the connection is not satisfactory, the user can always interrupt the transmission by clicking the 'Stop' command. In this case, the window stays in its initial state, reactivating the commands, which are deactivated during transmission, and deactivating the 'Stop' command. In the information window, the information concerning the interruption of the downloading process will be displayed.



C:\Mis documentos\Data1.xls

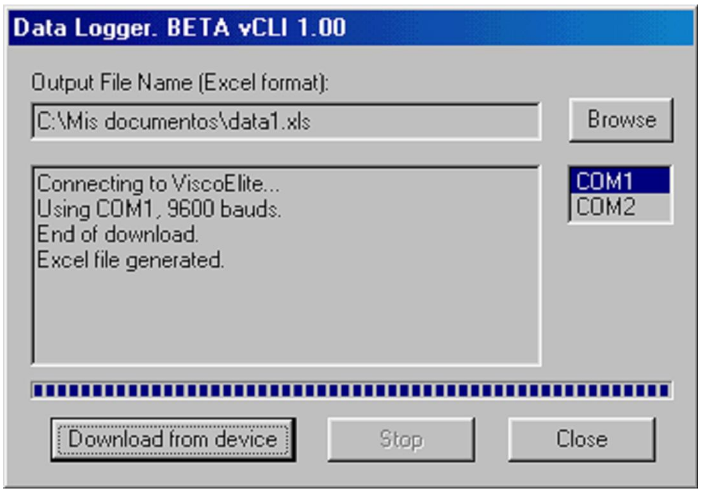
```
Connecting to ViscoElite...
Using COM1, 9600 bauds.
Download aborted.
```

In the case that the connection is satisfactory, the program will start the data download from the set. The program user will see the percentage of data received and its progress through the status bar on the lower-screen command bar. When the bar shows 100%, the program will generate the exit file with the path originally indicated. In the following screenshot you can observe the progress of the exit bar and the file generation process.



Output File Name (Excel format): C:\Mis documentos\data1.xls

```
Connecting to ViscoElite...
Using COM1, 9600 bauds.
```



Output File Name (Excel format): C:\Mis documentos\data1.xls

```
Connecting to ViscoElite...
Using COM1, 9600 bauds.
End of download.
Excel file generated.
```

Data Analysis

- Plot the apparent viscosity of polymer solution against the time of shearing. Compare the viscosity versus time for different shear rates.

- Plot the apparent viscosity of the examined polymer solution against the shear rate.

- Different models are used to describe the flow behavior of fluids. By fitting a model to the experimental data set, the flow behavior over wider than experimental range can be predicted. The number of free parameters of models, as well as the models' predictability varies. For instance, some models are more suitable for solutions of polymers with the broad MW distribution (gradual transition from Newtonian plateau to shear-thinning region) and some for narrow MW distribution polymers (sharp transition between Newtonian and shear-thinning regions).

Ostwald de Weale model (also: the power law model), given by Eq. 4, is the simplest model requiring two fitting parameters: κ and n. This model is capable of describing only Newtonian and shear-thinning (or shear-thickening) behavior. The logarithmic form of this model (Eq.9) is more suitable for the fitting procedure:

$$\log(\eta) = \log(\kappa) + (n-1)\log(\gamma) \tag{9}$$

The Cross model (Eq. 5) as well as some other three parameter models (e.g. the Carreau model given by Eq.10 and the Hamersma model given by Eq.11) are capable of describing Newtonian viscosity, shear-thinning (or shear-thickening) viscosity and also the transition between them with three adjustable parameters:

$$\eta = \frac{\eta_0}{\left(1 + \left(\frac{\gamma}{\gamma_1}\right)^2\right)^n} \tag{10}$$

$$\eta = \frac{\eta_\infty}{1 - \frac{\tau_2}{\tau}\left(1 - \exp(-H\tau)\right)} \tag{11}$$

where n and H – constants and γ_1 (or τ_1) and γ_2 (or τ_2) are the thresholds between I – II regions and II – III regions (see Fig. 3), respectively.

By the fitting of a straight line trend by the least squares method or by the non-linear least squares curve fitting (using the SciLab scripts available at the website of this course) calculate the constants for each of the models and analyze the obtained values.

- On the basis of the fitting of the parameters of Eqs (6), (7) and (8) to the experimental data (the relevant SciLab script is also available at the website of the course), determine which of the models describing the dependence between the shear stress and the shear rate is the most suitable for the description of the behavior of examined polymer solution.

Discussion

1. Assume that the solution of PAAm in water-glycerine solution can be treated as the athermal solution (ν=3/5). Try to classify the solution to the dilute or semidilute region additionally assuming that M=5·10^6 D and the C-C distance (the length of the C-C bound) is equal to 154 pm; hybridization sp^3. Neglect the solvent effects on the stiffness of the chain.

2. Is there a possibility to obtain the η_∞ value from the collected experimental results? Why?

3. What type of non-Newtonian behavior represents the studied polymer solution?

References/ Literature

1. A.Ya. Malkin "Rheology Fundamentals", Chem. Tec. Publishing. Canada ,1994

2. J. Lyklema " Fundamentals of Interface and Colloid Science", Vol. IV: Particulate Colloids" , Elsevier-Academic Press, 2005

3. J. F. Steffe "Rheological Methods in Food Process Engineering", Freeman Press, USA, 1996

4. J.E.Perrin, G.C.Martin *J.Chem.Educ*., **60**, 516 (1983)

5. http://www.youtube.com/watch?v=-RmamKIkpxs&feature=related achieved at 28.02.2012

Appendix A (written on the basis of [3])

In rotational viscometers of Searle type the moment of rotation (the torque) M required to rotate an immersed element (a spindle) in a fluid, at a constant angular velocity Ω, is measured. The torque is due to the shear stress τ, exerted on the spindle by the fluid. In the following derivation it is assumed that the flow is laminar, end and internal effects may be neglected and that there is no slip at the cylinder surfaces. If the spindle is of cylindrical shape, a force moment balance yields:

$$M = 2\pi\, r\, h\, r\, \tau = 2\pi\, r^2\, h\, \tau \qquad \text{(A-01)}$$

where r is any location in the fluid, that is:

$$R_S \leq \; r \leq R_C \qquad \text{(A-02)}$$

where R_s and R_c denote a radius of a spindle and of an outer cylinder (or container), respectively, and h is the spindle's height.

The shear stress at the wall of the spindle (r=R_c) is equal to:

$$\tau_S = \frac{M}{2\pi\,(R_S)^2\, h} \qquad \text{(A-03)}$$

The linear velocity v at r in terms of angular velocity ω is:

$$v = r\omega \qquad \text{(A-04)}$$

Hence, since the angular velocity is independent of r, we can write:

$$\frac{dv}{dr} = r\,\frac{d\omega}{dr} \qquad \text{(A-05)}$$

Let us notice that the flow velocity decreases with increasing distance from moving surface, therefore eq (A-05) can be written as:

$$\gamma = -\frac{dv}{dr} = -r\,\frac{d\omega}{dr} \qquad \text{(A-06)}$$

To relate the angular velocity to shear stress note that the torque is constant with the steady flow, so from eq. (A-01) we have:

$$r = \left(\frac{M}{2\pi\, h}\right)^{\frac{1}{2}} \tau^{-\frac{1}{2}} \qquad \text{(A-07)}$$

Differentiating of eq (A-07) with respect to the shear stress yields:

$$\frac{dr}{d\tau} = \left(\frac{M}{2\pi\, h}\right)^{\frac{1}{2}} \left(-\frac{1}{2}\tau^{-\frac{3}{2}}\right) \qquad \text{(A-08)}$$

Substituting the value of torque defined by eq (A-01) we obtain:

$$\frac{dr}{r} = -\frac{d\tau}{2\tau} \qquad \text{(A-09)}$$

Since the shear rate is a function of the shear stress, i.e. γ =f(τ), we can write:

$$\gamma = -r\frac{d\omega}{dr} = f(\tau) \qquad \text{(A-10)}$$

Thus, taking into account eq (A-09), we have:

$$d\omega = -\frac{dr}{r} f(\tau) = \frac{1}{2} \mathrm{f}(\tau)\left(\frac{d\tau}{\tau}\right) \qquad \text{(A-11)}$$

Integrating eq (A-11) we obtain a general expression for the angular velocity *Ω* of the spindle as a function of shear stress in the gap between the moving surface (where the angular velocity is equal to *Ω*) and the surface of outer cup (at which the angular velocity is zero), we obtain :

$$\Omega = -\frac{1}{2}\int_{\tau_\mathrm{s}}^{\tau_\mathrm{c}} f(\tau)\frac{d\tau}{\tau} \qquad \text{(A-12)}$$

where τ_c is the shear stress at the wall of outer container. The solution of the above equation depends on f(τ), which is determined by the properties of fluid. If the relationship between shear stress and shear rate for a given fluid is known, the eq (A-12) can be solved.

For a power law fluid this relationship is:

$$\gamma = \left(\frac{\tau}{\kappa}\right)^{\frac{1}{n}} \qquad \text{(A-13)}$$

and, when substituted into eq (A-12), it yields:

$$\Omega = \frac{n}{2\kappa^{\frac{1}{n}}}\left[(\tau_\mathrm{s})^{\frac{1}{n}} - (\tau_\mathrm{c})^{\frac{1}{n}}\right] \qquad \text{(A-14)}$$

Using eq (A-01) an alternative expression is obtained:

$$\Omega = \frac{n}{2\kappa^{\frac{1}{n}}}\left(\frac{M}{2\pi\,(R_\mathrm{s})^2 h}\right)^{\frac{1}{n}}\left[1 - \left(\frac{R_\mathrm{s}}{R_\mathrm{c}}\right)^{\frac{2}{n}}\right] \qquad \text{(A-15)}$$

Eq (A-15) reveals that the torque is not directly proportional to the spindle speed – it is strongly influenced by the exponent *n*.

Taking into account the force balance on the spindle (eq (A-01) the following expression for the shear rate in the case of power law fluid can be obtained:

$$\gamma = \mathrm{f}(r) = \left(\frac{M}{2\,\pi\, r^2\, h\, \kappa} \right)^{\frac{1}{n}} \qquad \text{(A-16)}$$

Then, the shear rate at the spindle is:

$$\gamma_\mathrm{s} = \mathrm{f}(R_\mathrm{s}) = \left(\frac{M}{2\,\pi\, (R_\mathrm{s})^2\, h\, \kappa} \right)^{\frac{1}{n}} \qquad \text{(A-17)}$$

Solving eq (A-15) for *M* and substituting the result into the above equation yields:

$$\gamma_\mathrm{s} = \frac{2\Omega}{n} \cdot \frac{(R_\mathrm{c})^{\frac{2}{n}}}{(R_\mathrm{c})^{\frac{2}{n}} - (R_\mathrm{s})^{\frac{2}{n}}} \qquad \text{(A-18)}$$

When $R_\mathrm{c} >> R_\mathrm{s}$ (as it is in the case of tests involving very large beakers) the above equation can be simplified to:

$$\gamma_\mathrm{s} = \frac{2\Omega}{n} \qquad \text{(A-19)}$$

Appendix B (Coaxial cylinders (rotational) viscometer)

These are the most widely used viscometers in laboratory and industrial applications. Their operational principle is based on the measurement of the force or torque required to rotate a spindle or bob (cylinder) at a specified speed in the sample (fluid) placed in another stationary cylinder, this torque being proportional to the viscosity of the fluid.

Fig. 3 schematically shows the design of a rotational viscometer. An inner cylinder 1 connected to a shaft 2 is placed inside an outer cylinder 4 filled with the fluid 3 which viscosity is to be measured. The inner cylinder is rotated at a constant speed by a synchronous motor 5 through gear 6. The outer cylinder is stationary. Fluid around the rotating cylinder starts to rotate. Since the fluid resists to the rotational movement due to its viscosity, the degree of spring 7 wounding is the measure of fluid viscosity.

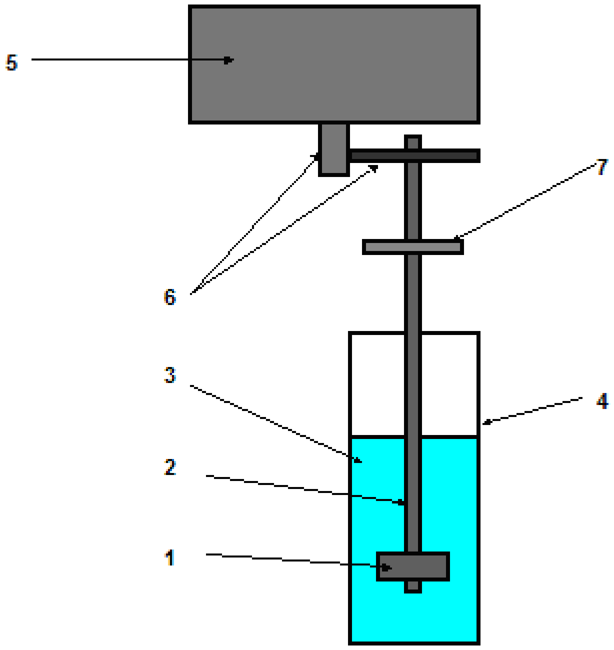


Fig. 3. The scheme of the rotational viscometer

Appendix C. SciLab Packets for estimation of parameters of some equations of the full rheological curve[5]

https://ciks.cbt.nist.gov/~garbocz/SP946/node8.htm

The header for all files

```
**************************************************************

clear
clc
File_name=input("..
Input name of the file with rheological data\n\n..
[The file should contain only numerical data organized in 6 columns!   ]\n..
[RPM     Viscosity     EOS     ShearStress     Temperature     Time]\n..
[============================================================
======]\n..
[It should be produced from oryginal .xls file created by viscometer   ]\n..
[software. All headers and comments in the .txt file should be removed!]\n..
\n","string");
[RR]=read(File_name,-1,6);
Nmax=length(RR)/6;

**************************************************************
```

The fitting procedures:

```
**************************************************************

//Carreau equation
//Lakatos I., Lakatos-Szabo J.,
//Acta Chim. Hung., 118, 147 (1985)
deff('y1=eta_A(p,x)','y1=p(1)/(1+(x/p(2))^2)^p(3)')
deff('e=D_eta_A(p,z)',..
   'eta_1=z(2),gamma_P=z(1),e=eta_1-eta_A(p,gamma_P)')
for i=1:Nmax,
   gamma_P(i)=RR(i,4)/RR(i,2);
   eta_1(i)=RR(i,2);
```

---

[5] https://ciks.cbt.nist.gov/~garbocz/SP946/node8.htm

```
    z(1,i)=RR(i,4)/RR(i,2);
    z(2,i)=RR(i,2);
end;
p1=[1000;10;-1];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
    eta_2(i)=eta_A(p2,gamma_P(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(gamma_P,eta_1,[-1]);
plot2d(gamma_P,eta_2,5);
mprintf("\nParameters of the Carreau equation");
mprintf("\n\neta0    = %f\n..
gammaP1 = %f\n..
n       = %f\n\n",p2(1),p2(2),p2(3));
mprintf("stdev    = %f\n",w);

****************************************************************

//Carreau-Yasuda equation
deff('y1=eta_A(p,x)','y1=(p(1)-p(2))*(1+(p(3)*x)^p(4))^((p(5)-1)/p(4))+p(2)')
deff('e=D_eta_A(p,z)',..
    'eta_1=z(2),gamma_P=z(1),e=eta_1-eta_A(p,gamma_P)')
for i=1:Nmax,
    gamma_P(i)=RR(i,4)/RR(i,2);
    eta_1(i)=RR(i,2);
    z(1,i)=RR(i,4)/RR(i,2);
    z(2,i)=RR(i,2);
end;
p1=[1000;10;1;1;1;1];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
   eta_2(i)=eta_A(p2,gamma_P(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(gamma_P,eta_1,[-1]);
plot2d(gamma_P,eta_2,5);
mprintf("\nParameters of the Carreau-Yasuda equation");
mprintf("\n\neta0    = %f\n..
etainf = %f\n..
```

```
lambda = %f\n..
a      = %f\n..
n      = %f\n\n",p2(1),p2(2),p2(3),p2(4),p2(5));
mprintf("stdev    = %f\n",w);

***********************************************************

//Cross equation
deff('y1=eta_A(p,x)','y1=(p(1)-p(2))/(1+p(3)*(x^p(4)))+p(2)')
deff('e=D_eta_A(p,z)',..
    'eta_1=z(2),gamma_P=z(1),e=eta_1-eta_A(p,gamma_P)')
for i=1:Nmax,
    gamma_P(i)=RR(i,4)/RR(i,2);
    eta_1(i)=RR(i,2);
    z(1,i)=RR(i,4)/RR(i,2);
    z(2,i)=RR(i,2);
end;
p1=[1000;1;1;0.1];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
   eta_2(i)=eta_A(p2,gamma_P(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(gamma_P,eta_1,[-1]);
plot2d(gamma_P,eta_2,5);
mprintf("\nParameters of the Cross equation");
mprintf("\n\neta0    = %f\n..
etainf  = %f\n..
K       = %f\n..
n       = %f\n\n",p2(1),p2(2),p2(3),p2(4));
mprintf("stdev    = %f\n",w);

***********************************************************

//Ellis equation
deff('y1=eta_A(p,x)','y1=p(1)/(1+(x/p(2))^(p(3)-1))')
deff('e=D_eta_A(p,z)',..
    'eta_1=z(2),tau=z(1),e=eta_1-eta_A(p,tau)')
for i=1:Nmax,
    tau(i)=RR(i,4);
```

```
    eta_1(i)=RR(i,2);
     z(1,i)=RR(i,4);
    z(2,i)=RR(i,2);
end;
p1=[1000;10;10];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
   eta_2(i)=eta_A(p2,tau(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(tau,eta_1,[-1]);
plot2d(tau,eta_2,5);
mprintf("\nParameters of the Ellis equation");
mprintf("\n\neta0    = %f\n..
ro2     = %f\n..
alfa    = %f\n\n",p2(1),p2(2),p2(3));
mprintf("stdev    = %f\n",w);

************************************************************

//Meter equation
deff('y1=eta_A(p,x)','y1=p(1)+(p(2)-p(1))/(1+(x/p(3))^(p(4)-1))')
deff('e=D_eta_A(p,z)',..
    'eta_1=z(2),tau=z(1),e=eta_1-eta_A(p,tau)')
for i=1:Nmax,
    tau(i)=RR(i,4);
    eta_1(i)=RR(i,2);
    z(1,i)=RR(i,4);
    z(2,i)=RR(i,2);
end;
p1=[10;1000;10;10];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
    eta_2(i)=eta_A(p2,tau(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(tau,eta_1,[-1]);
plot2d(tau,eta_2,5);
mprintf("\nParameters of the Meter equation");
mprintf("\n\netainf    = %f\n..
```

```
eta0    = %f\n..
ro2     = %f\n..
alfa    = %f\n\n",p2(1),p2(2),p2(3),p2(4));
mprintf("stdev    = %f\n",w);

*****************************************************************

//Powell_Eyring equation
deff('y1=eta_A(p,x)','y1=p(1)+(p(2)-p(1))*asinh(p(3)*x)/(p(3)*x)')
deff('e=D_eta_A(p,z)',..
    'eta_1=z(2),gamma_P=z(1),e=eta_1-eta_A(p,gamma_P)')
for i=1:Nmax,
    gamma_P(i)=RR(i,4)/RR(i,2);
    eta_1(i)=RR(i,2);
    z(1,i)=RR(i,4)/RR(i,2);
    z(2,i)=RR(i,2);
end;
p1=[10;1000;1];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
    eta_2(i)=eta_A(p2,gamma_P(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(gamma_P,eta_1,[-1]);
plot2d(gamma_P,eta_2,5);
mprintf("\nParameters of the Powell-Eyring equation");
mprintf("\n\netainf  = %f\n..
eta0    = %f\n..
tauc    = %f\n\n",p2(1),p2(2),p2(3));
mprintf("stdev    = %f\n",w);

*****************************************************************

//power law
deff('y1=eta_A(p,x)','y1=(p(1)*x^(p(2)-1))')
deff('e=D_eta_A(p,z)',..
    'eta_1=z(2),gamma_P=z(1),e=eta_1-eta_A(p,gamma_P)')
for i=1:Nmax,
    gamma_P(i)=RR(i,4)/RR(i,2);
    eta_1(i)=RR(i,2);
```

```
    z(1,i)=RR(i,4)/RR(i,2);
    z(2,i)=RR(i,2);
end;
p1=[1;1];
[p2,err]=datafit(D_eta_A,z,p1,'qn');
for i=1:Nmax,
    eta_2(i)=eta_A(p2,gamma_P(i));
end;
w=st_deviation(eta_1-eta_2);
plot2d(gamma_P,eta_1,[-1]);
plot2d(gamma_P,eta_2,5);
mprintf("\nParameters of the power-law equation\n");
mprintf("\n\kappa   = %f\n..
n      = %f\n\n",p2(1),p2(2));
mprintf("stdev    = %f\n",w);

***************************************************************

//viscoplastic models
deff('y1=tau_A(p,x)','y1=p(1)*x^p(2)+p(3)')
deff('e=D_tau_A(p,z)',..
    'tau_1=z(2),gamma_P=z(1),e=tau_1-tau_A(p,gamma_P)')
for i=1:Nmax,
    gamma_P(i)=RR(i,4)/RR(i,2);
    tau_1(i)=RR(i,4);
    z(1,i)=RR(i,4)/RR(i,2);
    z(2,i)=RR(i,4);
end;
p1=[1;1;1];
[p2,err]=datafit(D_tau_A,z,p1,'qn');
for i=1:Nmax,
    tau_2(i)=tau_A(p2,gamma_P(i));
end;
w2=st_deviation(tau_1-tau_2);
plot2d(gamma_P,tau_1,[-1]);
mprintf("\nHershel-Bulkley model\n");
plot2d(gamma_P,tau_2,5);
mprintf("\n\kappa    = %f\n..
n      = %f\n..
tauy    = %f\n\n",p2(1),p2(2),p2(3));
```

```
mprintf("stdev    = %f\n",w2);
coefs1=regress(gamma_P,tau_1);
for i=1:Nmax,
tau_3(i)=coefs1(2)*gamma_P(i)+coefs1(1);
end;
w3=st_deviation(tau_1-tau_3);
mprintf("\nBingham model\n");
plot2d(gamma_P,tau_3,6);
mprintf("\n\kappaB    = %f\n..
tauy    = %f\n\n",coefs1(2),coefs1(1));
mprintf("stdev    = %f\n",w3);
coefs2=regress(sqrt(gamma_P),sqrt(tau_1));
for i=1:Nmax,
tau_4(i)=(coefs2(2)*sqrt(gamma_P(i))+coefs2(1))^2;
end;
w4=st_deviation(tau_1-tau_4);
mprintf("\nCason model\n");
plot2d(gamma_P,tau_4,7);
mprintf("\n\kappaC    = %f\n..
tauy    = %f\n\n",coefs2(2),coefs2(1)^2);
mprintf("stdev    = %f\n",w4);

*****************************************************************
*****************************************************************

//Herschel-Bulkley equation
deff('y1=tau_A(p,x)','y1=p(1)*x^p(2)+p(3)')
deff('e=D_tau_A(p,z)',..
    'tau_1=z(2),gamma_P=z(1),e=tau_1-tau_A(p,gamma_P)')
File_name=input("Name of the file with..
 rheological data tau=f(gammaP)\n","string");
[RR]=read(File_name,-1,2);
Nmax=length(RR)/2;
for i=1:Nmax,
    gamma_P(i)=RR(i,1);
    tau_1(i)=RR(i,2);
    z(1,i)=RR(i,1);
    z(2,i)=RR(i,2);
end;
p1=[1;1;1];
```

```
[p2,err]=datafit(D_tau_A,z,p1,'gc');
for i=1:Nmax,
    tau_2(i)=tau_A(p2,gamma_P(i));
end;
plot2d(gamma_P,tau_1,[-1]);
plot2d(gamma_P,tau_2,5);
format('e',15);p2
```