

On the viscosity of polymer solutions

Theoretical background: Thomas G. Mezger: *The Rheology Handbook*, Vincentz Network, 4th Edition.

Type of practice: Individual.

Aim of practice: To determine the intrinsic viscosity of a polymer solution and, based on that, derive its viscosity average molar mass.

1 Introduction

1.1 Macromolecular solutions

Nowadays, different polymers are widely used in applications (e.g. cosmetics and personal care products, essential components of drug delivery vehicles, etc.). The viscosity of creams and pastes are frequently adjusted by adding various polymers. They are even applied to modify the delivery and release of drugs.

Macromolecules are giant molecules which are built up from a large number of repeating units (i.e., monomers) linked by covalent bonds. Their relative molecular mass (M_r) is usually above 10 000. Their chemical structure shows a great variability (e.g. linear or cross-linked molecular chains, different functional groups, etc.) and thus their properties do so as well. Macromolecules can be dissolved in appropriate solvents, but the solubility dramatically decreases with growing molecular mass. Compared to the small molecule materials, polymers typically dissolve very slowly. The solvent molecules penetrating into the solid particles solvate (in water hydrate) the molecule chains. The volume of the particles grows, i.e., they swell, and the swelling turns *unlimited*. At this stage the solvated chains become free and the individual polymer coils move away in the solution. By the end, *colloidal solution* forms in which the macromolecules exhibit a homogeneous spatial distribution.

Many physico-chemical properties of polymers are investigated in solution which are typically different from those in solutions of small molecule compounds. One important difference is that their molecular mass cannot be expressed as a single value. The molecular mass is characterized by a distribution even in the case of relatively monodisperse sample (i.e., when the macromolecule size falls within a narrow interval). Osmotic pressure, light scattering, sedimentation in centrifuge, and viscosity are frequently measured properties of polymer solutions in order to determine their molecular mass and in some cases its distribution. Different molecular mass can be derived from those properties, such as number-average from the concentration dependence of osmotic pressure, mass-average from light scattering, and the so called Z-average from sedimentation rate.

By their structure, we classify the water soluble macromolecules as:

- non-ionic macromolecules, which are hydrophilic polymers frequently containing hetero atoms in the chain (e.g. polyethylene oxide, polyethylene glycol (PEG)), and
- ionic macromolecules or so called polyelectrolytes, which contain chemically bonded functional groups which can undergo dissociation / protonation, thus can become locally charged.

According to their functional groups, polyelectrolytes can be anionic (i.e. acidic, e.g., $-\text{COO}^-$, polyacrylic acid), cationic (i.e., alkaline, e.g. $-\text{NH}_3^+$, polyethyleneimine), and amphoteric (e.g., proteins and gelatin). Their overall charge depends on the functional groups, on the *pH* of the medium, and on the type and concentration of other electrolytes in the system. Upon dissociation / protonation of the functional groups, the polymer coils achieve a net charge which is neutralized by counter ions. These effects influence the conformation of unique polymer coils and thus the viscosity of polymer solutions.

1.2 Viscosity

Viscosity, or so called internal friction measures how much a fluid (gas or liquid) stands against the shear stress (or drag) which would make the fluid move.

The flow field within a tube (capillary) is illustrated in Fig. 1. Laminar flow evolves provided that the flow rate is not too high. This can be imagined as a medium divided into infinite number of coaxial cylinders moving parallel with respect to each other. The motion of fluid particles on the microscale is parallel to the macroscopic flow direction, thus the layers cannot mix with each other. However, the propagation velocity of the coaxial layers depends on the distance to the boundary (e.g., to the tube wall; see the different lengths of black arrows in Fig. 1). Provided that the motion of the coaxial cylinder layers is parallel and steady, the internal friction force opposing the motion (F) is linearly proportional to the area of the slipping layers (A) and to the velocity gradient (or shear rate γ ; in two dimensions, considering the longitudinal cross section of the tube: du/dy , i.e., to the change of flow velocity per unit distance). The proportionality factor characteristic to the given fluid is its dynamic viscosity (η):

$$F = \eta A \frac{du}{dy}. \quad (1)$$

Introducing $F/A = \tau$ shear stress and $du/dy = \gamma$ notations:

$$\tau = \eta \gamma, \quad (2)$$

which is known as the Newtonian law of viscosity. It validly describes the behavior of so called Newtonian fluids (gases and liquids of small molecules). SI unit of τ is N/m^2 , which is frequently called Pa, however, it is not a pressure (since the force is not perpendicular to the surface) but a stress (because the force is parallel to the surface). SI unit of γ is velocity/distance, i.e., $(\text{m/s})/\text{m} = \text{s}^{-1}$. Hence the unit of dynamic viscosity is $\text{Pa} \cdot \text{s}$.

1.2.1 Capillary viscometry

The simplest way to determine the viscosity of a Newtonian liquid is to measure the time it takes for the liquid to flow through an Ostwald type capillary viscometer (Fig. 2). Hagen–Poiseuille law states that the volumetric flow rate (Q , i.e., the ratio of the liquid volume V to the time t required for passing through the capillary) depends both on the capillary geometry and on the properties of the liquid:

$$Q = \frac{V}{t} = \frac{\pi R^4}{8L\eta} \Delta p, \quad (3)$$

where R and L are the radius and length of the capillary, respectively, $\Delta p = \rho g h$ is the hydrostatic pressure difference (h is the difference in liquid column heights between the two sides, g is gravitational acceleration, and ρ is liquid density), and η is the dynamic viscosity. Under the same conditions (same capillary and passing volume) and after merging the constants:

$$t_{\text{flow}} = k \frac{\eta}{\rho} = k \eta_{\text{kin}}, \quad (4)$$

where η_{kin} is the so called kinematic viscosity. Even though the capillary constant k can be determined after careful calibration (applying a liquid of known η and ρ), and thus the kinematic viscosity of an other liquid

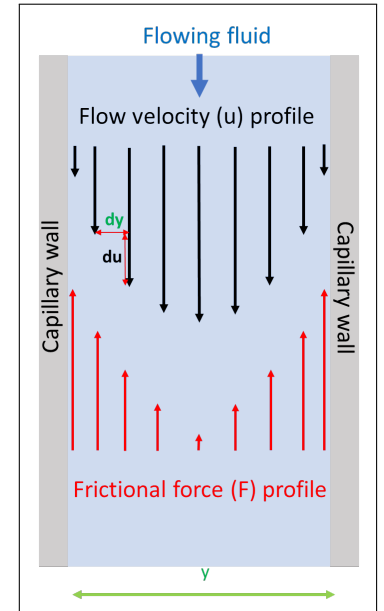


Figure 1: Flow profile in a tube (capillary).

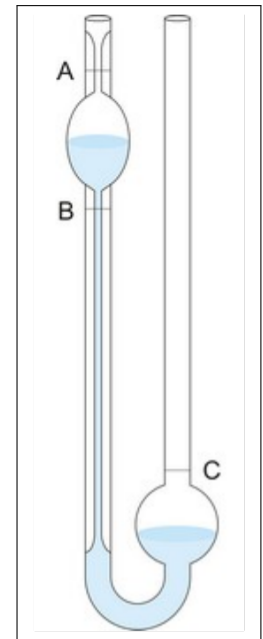


Figure 2: Sketch of an Ostwald type capillary viscometer.

can be directly measured, this tool is mostly used in practice for relative measurements. Considering two liquids (e.g., two solutions of different concentration)

$$\frac{t_1}{t_2} = \frac{\eta_{\text{kin},1}}{\eta_{\text{kin},2}} = \frac{\eta_1 \rho_2}{\eta_2 \rho_1}. \quad (5)$$

If the solution is dilute, and its density can be taken closely equal to that of solvent, then the ratio of the times required for flowing through the capillary (and thus the ratio of the kinematic viscosities) approximately equals the ratio of the dynamic viscosities:

$$\frac{t_{\text{solution}}}{t_{\text{solvent}}} = \frac{\eta_{\text{kin, solution}}}{\eta_{\text{kin, solvent}}} \approx \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} = \eta_{\text{rel}}, \quad (6)$$

where η_{rel} is the relative viscosity of the solution in comparison to the dynamic viscosity of the solvent.

1.3 Viscosity of polymer solutions

The simplest way to determine the relative viscosity of appropriately dilute polymer solutions (i.e., exhibiting Newtonian behavior) is to measure their flow-through times in an Ostwald type capillary viscometer.

According to the Einstein equation, the relative viscosity (η_{rel}) of a solution containing sphere-like colloid particles (e.g., distinct polymer coils) depends only on the volume fraction of the particles (ϕ):

$$\eta_{\text{rel}} = 1 + 2.5\phi. \quad (7)$$

The volume fraction of the polymer $\phi = V_{\text{polymer}}/V_{\text{solution}}$ can be calculated if the volume of the solution (V_{solution}) and that of the polymer (V_{polymer}) are known. This latter one is expressed by the mass of the polymer (m , [g]) and its coil density (ρ_c , [g/cm^3]):

$$\phi = \frac{(m/\rho_c)}{V_{\text{solution}}} = \frac{(m/V_{\text{solution}})}{\rho_c} = \frac{c_{\text{polymer}}}{\rho_c}, \quad (8)$$

where c_{polymer} is the mass concentration of the polymer solution (g/cm^3). After substituting the above expression into equation (7) we come to

$$\eta_{\text{rel}} = 1 + 2.5 \frac{c_{\text{polymer}}}{\rho_c}, \quad (9)$$

which can be rearranged as

$$\frac{\eta_{\text{rel}} - 1}{c_{\text{polymer}}} = \frac{2.5}{\rho_c} = \frac{\eta_{\text{sp}}}{c_{\text{polymer}}}, \quad (10)$$

where $\eta_{\text{sp}} = (\eta_{\text{solution}} - \eta_{\text{solvent}})/\eta_{\text{solvent}}$ is the specific viscosity. Equation (10) is only valid in infinitely dilute solutions, where the macromolecules do not interact with each other while the liquid flows. This can be considered as a limit value upon extrapolation to zero concentration. Plotting $\eta_{\text{sp}}/c_{\text{polymer}}$ values as a function of polymer concentration and extrapolating to zero concentration yields the so called limiting (or intrinsic) viscosity, which is characteristic to the solute – solvent system ($[\eta]$, Fig. 3):

$$\lim_{c_{\text{polymer}} \rightarrow 0} \frac{\eta_{\text{sp}}}{c_{\text{polymer}}} = [\eta] = \frac{2.5}{\rho_c}. \quad (11)$$

Equation (11) reveals that the viscosity increase observed upon dissolution of polymers is reversely proportional to the average coil density ρ_c . Consequently, compact polymer coils characterized with large coil density modify less on viscosity, whereas properly solvated, loose coils interact with each other which decreases the tendency of the liquid to flow, i.e., increases the viscosity. According to the Kuhn root law

$$\rho_c = K_p (M_r)^{-1/2}, \quad (12)$$

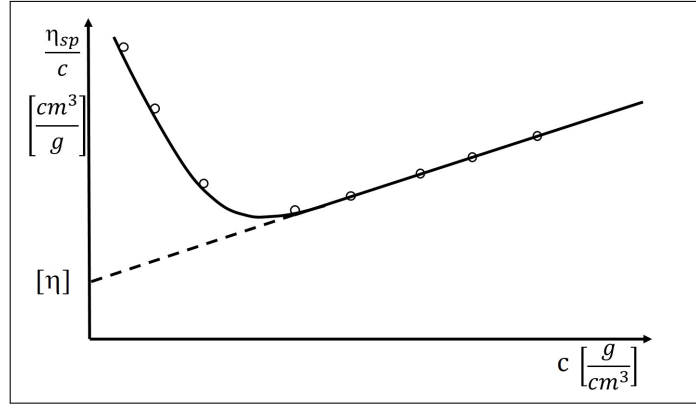


Figure 3: Determination of intrinsic viscosity $[\eta]$ via graphical extrapolation.

where K_p is a constant characteristic to the polymer. That is, the coil density decreases with increasing relative molecular mass, because the macromolecular chain cannot be kept compact anymore by the intramolecular van de Waals interactions. Therefore the polymer coil uncoils more and more. By merging equations (11) and (12) we obtain a formula applicable for the determination of molecular mass:

$$[\eta] = \frac{2.5}{K_p (M_r)^{-1/2}} = K_\eta (M_r)^{1/2}, \quad (13)$$

which is known as Kuhn law of viscosity and is valid for polymer solutions in Θ -state. In Θ -state the polymer coil is interaction free, thus it is considered as a quasi ideal state. Under such conditions, the solvent – polymer and polymer – polymer interactions compensate each other, and the extension of the coil is only dictated by the chemical structure and its chain flexibility. If the polymer is not in such ideal state upon dissolution in the given solvent (solvent mixture), because solvation results in excessive uncoiling, coil density ρ_c decreases and the exponent overcomes $1/2$. In such cases, a new exponent (a) replaces the original $1/2$ value, which describes the *appropriateness* of the solvent (i.e., the extent of solvation). Limiting viscosity can be expressed at any extent of solvation by applying the Kuhn–Mark–Houwink equation:

$$[\eta] = K_\eta (M_r)^a. \quad (14)$$

Exponent a is a constant describing the solvent – polymer interactions, whose value is usually in the range of $0.5 - 0.85$, and K_η is another constant depending on the polymer. Those constants are tabulated in various polymer textbooks for many polymer – solvent pairs. A few of them are gathered in Table 1.

To wrap-up, by measuring the flow-through times for the solvent and for polymer solutions of different concentration (c_{polymer}), t_{solvent} and t_{solution} , respectively, $\eta_{\text{sp}}/c_{\text{polymer}}$ values can be obtained, which results in the determination of intrinsic viscosity $[\eta]$ if plotted as a function of c_{polymer} (Fig. 3). From the intrinsic viscosity, provided that the appropriate numerical constants are known, the viscosity average relative molecular mass can be derived.

Table 1: Constants of Kuhn–Mark–Houwink equation for various polymer solutions.

Polymer	Solvent	t (°C)	K_η (cm ³ /g)	a
Polyethylene	Xylene	75	$1.35 \cdot 10^{-2}$	0.74
Polystyrene	Toluene	30	$1.20 \cdot 10^{-2}$	0.72
PMMA	Methyl ethyl ketone	25	$0.58 \cdot 10^{-2}$	0.72
PVA, PEG	Water	25	$4.28 \cdot 10^{-2}$	0.64
Epoxy resin	Dioxane	25	$3.98 \cdot 10^{-2}$	0.61

2 Experimental

Weight in a given amount (3.5–7.5 g) of the polymer sample (PEG) into a 100 cm³ beaker and add 50 cm³ distilled water with a graduated cylinder. *If the instructor does not state otherwise*, weight in 6.0 g of PEG. Homogenize the system with a glass rod. *Important notice: Polymers dissolve slowly, they mostly swell at first. Do not stir or shake the solution rigorously because foam may form.* After the complete dissolution of PEG, prepare a dilution series. The concentration of each solution must be 65–80% of the previous one. *If the instructor does not state otherwise*, the concentration of each solution must be 80% of the previous one. When preparing the dilution series, pipette the *unwanted* solution portion into a clean and dry beaker for later measurements, then add distilled water to the remaining solution to reach the aimed concentration in 50 cm³ volume. During calculation, consider the volume additive. For easier solution preparation, use automatic pipette. *If the instructor does not state otherwise*, you will need the stock polymer solution, and its 8 dilutions, and distilled water for the measurements.

Measure the relative viscosity of the prepared dilution series by pipetting 5–5 cm³ portions into the Ostwald type capillary viscometer. Before the first measurement, thoroughly flush the viscometer with distilled water; suck 100 cm³ water through the capillary using water suction pump. Pipette 5 cm³ of the given solution into the thicker channel of the viscometer (Fig. 2C). Applying the rubber suction ball, lift the solution level above the upper sign of the viscometer (Fig. 2A). Be careful, the solution should not penetrate into the plastic tubing. Then, let the liquid flow and observe how the meniscus descends. Measure the flow-through time; start the stopwatch when the meniscus reaches the upper sign (Fig. 2A) and stop it when the meniscus reaches the lower one (Fig. 2B). First measure the flow-through time for distilled water (t_{solvent}); repeat the measurement twice. Afterwards, measure the flow-through time for the samples of the dilution series (t_{solution}) according to the increasing concentration. Finally, measure the flow-through time for the stock solution as well. *If the instructor does not state otherwise*, the flow-through time measurements must be repeated once more by lifting up the meniscus of the just measured 5 cm³ solution once more, i.e., no need to change the solution.

3 Evaluation of the measured data

1. Calculate the relative and specific viscosity of the solutions, and summarize the results according to Table 2.

Table 2: Results of capillary viscometry.

PEG solutions		$t_{\text{flow}} / \text{s}$				η_{rel}	η_{sp}	$\eta_{\text{sp}}/c_{\text{polymer}}$
	$c_{\text{polymer}} / (\text{g}/\text{cm}^3)$	1.	2.	3.	average	–	–	–
solvent						–	–	–
1.								
⋮								

2. Plot $\eta_{\text{sp}}/c_{\text{polymer}} - c_{\text{polymer}}$ function. Derive the intrinsic viscosity and its standard deviation (see Appendix; Excel LIN.EST, Origin, QtiPlot, etc.) by linearly fitting the appropriate part of the measured data and performing extrapolation to zero polymer concentration. Calculate the viscosity average relative molecular mass of PEG and its standard deviation (see Appendix: Error spreading) applying the constants in Table 1 and equation (14). Interpret the results in the view of literature data; add the literature source as well.

Questions

1. What kind of macromolecules are able to dissolve in water and which can only swell? List 1–1 example.
2. Which properties of macromolecular solutions are suitable for the determination of average molecular mass? Why only the average molecular mass can be obtained such way?
3. What is Newtonian liquid? List two examples.
4. What is shear stress? (definition, notation, unit)
5. What parameters influence the viscosity of polymer solutions and what is the typical difference between the viscosity of macromolecular and regular (small molecules) solutions?
6. How do you obtain the intrinsic viscosity of a solution and what is its relation to the average molecular mass of polymers?
7. Briefly describe how Ostwald type viscometer works.
8. A PEG stock solution is made by weighting in 5 g of PEG into a beaker and adding 50 cm³ of distilled water. How to prepare 50 cm³ solution by diluting from this stock solution, if its concentration must be 65 % of the stock solution?
9. The intrinsic viscosity of aqueous PEG solutions is found to be 19.7 cm³ g⁻¹. For such system, $K_{\eta} = 4.28 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.64$. What is the viscosity average relative molecular mass of the used PEG sample?