Exercise 10

DETERMINATION OF THE VISCOSIMETRIC AVERAGE MOLAR MASS OF POLYMERS

(UWAGA! Zostawiłam numerację wzorów taką jak w oryginalnym ćwiczeniu dla ułatwienia sprawdzania merytorycznej poprawności! Po zatwierdzeniu takiej wersji opisu pozmieniam numerowanie wzorów)

Issues: internal friction, viscosity, viscosity measurement methods with particular emphasis on the capillary method, physicochemical properties of polymer solutions (conformation of macromolecules in solution, diffusion in solutions of macromolecules, viscosity of macromolecular solutions, dependence of the limit viscosity number on the molar mass of the polymer). Fluid viscosity η is defined as the proportionality coefficient in Newton's equation:

$$F = \eta A \frac{dv}{dx}$$

Where *F* is the force applied to surface *A* parallel to the direction of flow needed to give the fluid a *dv/dx* velocity gradient. The gradient is set perpendicular to the flow direction. Viscosity is characteristic of a given fluid and, as Newton's equation assumes, does not depend on the velocity gradient.

Here, we will limit ourselves to laminar flow in a liquid. Newton's assumption is satisfied in principle by all real solutions and by some dispersion systems. Such systems are called Newtonian fluids. The others (non-Newtonian fluids) include, among others, some sols and solutions of macromolecules. Although the solutions of macromolecules are real solutions, they are sometimes classified as microdispersion systems - colloidal systems due to the fact that the sizes of polymer coils in the solution fall within the limits set by the definition of colloidal systems. The introduction of particles with dimensions larger than its particles into the liquid causes a partial inhibition of mutual sliding of the liquid layers (Fig. 1), and consequently an increase in the viscosity of the system.

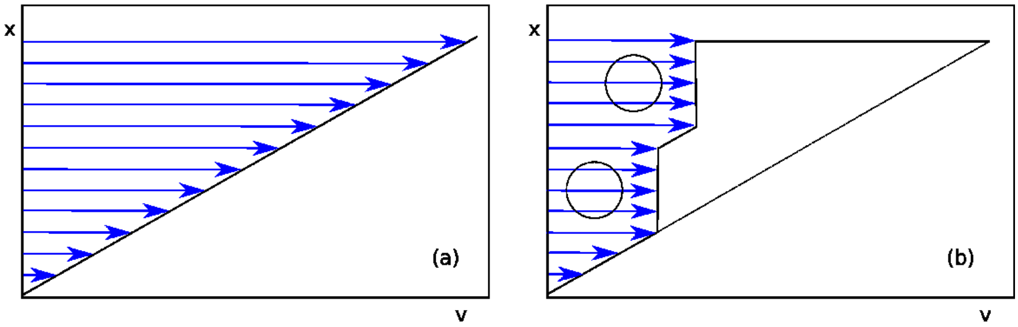


Fig. 1. Influence of the presence of rigid particles on the fluid velocity gradient. (a) flow in pure solvent, (b) flow in the presence of large particles.

The viscosity of a dilute solution of rigid particles is given by Einstein's equation:

$$\eta = \eta_0(1 + \Phi'\varphi) \quad (1)$$

where η_0 – viscosity of the solvent, η – viscosity of the solution, φ – volume fraction of particles (the ratio of the sum of their volumes to the volume of the solution), Φ' – coefficient depending on the shape of the particles equal to 2.5 for spherical particles. Equation (1) can be easily transformed into:

$$\Phi'\varphi = \frac{\eta-\eta_0}{\eta_0} \quad (2)$$

For a monodisperse system (expressing the concentration of particles as the ratio of their mass to the volume of the system, i.e. $\rho_p = Nm_c/V_u$, where N – number of particles, m_c – particle mass, V_u – volume of the system) from equation (1) one obtains:

$$\frac{\eta-\eta_0}{\eta_0\,\rho_p} = \frac{\Phi' V_c}{m_c} \quad (3)$$

where V_c is the volume of the particle. Equation (3) describes the viscosity of a dispersion system containing rigid particles. If the system under consideration is a polymer solution, then the mass of a single particle (m_c) is equal to the mass of one particle, and the product of this mass and the Avogadro numer N_A gives the molar mass M of the polymer, so:

$$\frac{\eta-\eta_0}{\eta_0\,\rho_p} = \frac{\Phi'' V_c}{M} \quad (4)$$

where $\Phi'' = N_A\Phi'$.

Equation $(\eta - \eta_0)/\eta_0\rho_p$ is commonly called the viscosity number. As can be seen from equation (4), it could be used to determine the molar mass of the polymer, if its solution could be treated as a dispersion of rigid, uniform bodies. The conformation of macromolecules in solutions, however, is generally too complicated to apply the simple assumption of rigid bodies. For the sake of simplicity, considering linear polymers (composed of molecules without branches, not cross-linked) that do not tend to adopt specific structures (such as protein molecules), one can assume that the structure of a macromolecule in solution resembles a disordered, tangled bundle. This ball is to some extent penetrated by solvent molecules and is in constant motion consisting in the constant change of its conformation. In addition, the coil also performs disordered translational and rotational movements in the solution. Therefore, there is always a certain probability that two or more polymer coils may penetrate each other. In this situation, the measure of the "undisturbed" size of the ball will not be the viscosity number, but its value extrapolated to the polymer concentration equal to 0 (i.e. a highly diluted solution), called the limiting viscosity number $[\eta]$:

$$[\eta] = \lim_{\rho_p \to 0} \frac{\eta - \eta_0}{\eta_0 \rho_p} \qquad (5)$$

Euation (4) should be writen:

$$[\eta] = \frac{\Phi'' V_c}{M} \qquad (6)$$

The shape of the polymer coil in the solution is the result of the possibility of rotation of successive segments around single intersegment bonds. Due to the need to maintain the angles between these bonds, the position of two successive segments of the polymer is strongly interdependent. This condition weakens with increasing distance between the positions of the considered segments in the polymer chain. The position of two distant segments depends almost only on the length of the chain connecting them. Bearing in mind that the segments make constant movements, one may ask whether there is a way to determine the average density of the segments around the center of gravity of the polymer coil. If the change in the energy of interactions between the solvent molecules and their surroundings during the transition from a pure solvent to a polymer solution is compensated by an appropriate increase in the entropy of the system (the free enthalpy of mixing the solvent with the polymer is equal to zero), then the polymer segments will be surrounded by both other segments and and solvent particles. A solvent selected in such a way that the above condition is met is called a theta solvent, the obrained solution is a perfect solution.

[U5]The relation between the limiting viscosity number and the polymer molecular mass is described by Mark-Kuhn-Houvink-Sakurada equation:

$$[\eta] = KM^c \qquad (12)$$

where *K, c* – constants depending on the type of polymer and solvent, with the value of c increasing as the solubility of the polymer increases. The constant c assumes values in the range of 0.5 to 0.8 for flexible chains and close to 1 for stiffened chains forming bundles impenetrable to the solvent.

To calculate the molar mass from equation (12), a [η] value must be initially determined. However, an unambiguous determination of the limit in equation (5) is not possible unless the general relationship between the viscosity number and the concentration of the polymer is known. The Flory-Huggins theory results in a relationship called the Huggins equation:

$$\frac{\eta - \eta_0}{\eta_0 \, \rho_p} = [\eta] + A\rho_p + B\rho_p^2 + C\rho_p^3 + \cdots \qquad (16)$$

where A, B, C... constants depending on the type of polymer and solvent. The individual components of equation (16) correspond to the influence on the viscosity of the system: the presence of single polymer molecules, the presence of aggregates composed of two polymer molecules, etc. Assuming that viscosity measurements are made for diluted polymer solutions (in which case the probability of interactions between polymer molecules decreases very quickly together with the number of molecules interacting with each other) you can truncate all terms of the sum except the first two to obtain a linear equation of a straight line:

$$\frac{\eta-\eta_0}{\eta_0\,\rho_p} = [\eta] + A\rho_p = [\eta] + k'[\eta]^2\rho_p \qquad (17)$$

where k' – Huggins coefficient taking a value close to 0.6 for solutions Θ and lower when $\chi < 0{,}5$.

One of the viscosity measurement methods is the so-called capillary method, which consists in measuring the flow time of a liquid through a narrow tube (capillary). In practice, the volume of liquid that has flowed through the capillary in time t is measured. The viscosity number can be determined from relative measurements, i.e. by performing analogous measurements in relation to the tested and standard liquid:

$$\frac{\eta-\eta_0}{\eta_0\,\rho_p} = \frac{\rho t-\rho_0 t_0}{\rho_0 t_0 \rho_p} \qquad (21)$$

(indices 0 refer to the solvent). As we assumed above, we only consider dilute solutions of the polymer, so $\rho \approx \rho_0$, and equation (21) can be written as:

$$\frac{\eta-\eta_0}{\eta_0\,\rho_p} = \frac{(t/t_0)-1}{\rho_p} \qquad (22)$$

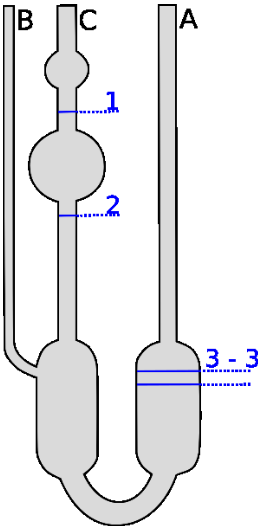
When designing viscosity measurements to determine the molar mass of a polymer, it should be remembered that the considerations carried out above refer to laminar flow and that solutions of macromolecules are non-Newtonian fluids. Measurements using a capillary viscometer give correct results if the flow rate (and therefore the shear stress causing deformation of the polymer coil, which in turn changes the viscosity of the solution) is not too high. Practice shows that this condition is met with a flow time of 3 - 5 minutes from a typical Ubbelohde viscometer.

Experimental

The aim of the exercise is to determine the viscosimetric average molar mass of a selected polymer

Preliminary steps

- Turn on the ultrathermostat and set the temperature to 25 °C.
  - Remember to ensure the supply of cold tap water to the thermostat
  - The cold water tap should be turned on gently - so that no bulge appears on the inlet hose
- Filter the appropriate amount of the starting poly-(vinyl alcohol) solution and prepare solutions with concentrations $1{,}00\cdot10^{-2}$, $0{,}80\cdot10^{-2}$, $0{,}60\cdot10^{-2}$, $0{,}40\cdot10^{-2}$ and $0{,}20\cdot10^{-2}$ g/cm^3.
- Rinse the viscometer (fig. 2) with distilled water:
  - pour water into arm A,
  - by plugging arm B, draw liquid into arm C using the pump
  - when the water drains from arm C, remove it using a hose inserted into arm A and connected to the water pump
  - repeat rinsing several times.



Rys. 2. Ubbelohde viscosimeter

Viscosity measurements

Viscosity measurements should be carried out successively for the solvent (distilled water) and poly-(vinyl alcohol) solutions of increasing concentrations.

Between measurements, the viscometer should be rinsed with the next test solution in a manner analogous to the initial washing with water.

- Introduce the tested liquid into the A arm of the viscometer so that its level is between the lines 3-3 on the A arm of the viscometer
- Using the pump, draw the liquid up to the tank D (at the same time blocking the outlet of the arm B).

- Disconnect the water pump and observe the descent of the meniscus.
- Measure the meniscus descent time from line 1 to line 2.
- Perform the measurement 3 times. Record the results in table 1
- If successive results for a given concentration decrease, it means that the tested liquid has not yet reached the set temperature. Then wait a few minutes and repeat the measurements.
- After the measurements, remove the solution from the viscometer using a water pump, rinse the viscometer several times with distilled water and leave it filled with water.

Tabela 1. Wyniki

Solution concentration ρ_p [g/cm^3]	Liquid flow time [s]	Mean liquid flow time [s]	Viscosity number [cm^3/g]
0	....	....	–
$0{,}20\cdot10^{-3}$	....	....	....
…			

Calculations

- On the basis of the obtained experimental results, calculate the average outflow time of each of the tested liquids
- Basing on equation (22) calculate the viscosity number ($(\eta - \eta_0)/\eta_0\rho_p$)
- Plot the dependency $(\eta - \eta_0)/\eta_0\rho_p = f(\rho_p)$
- Using the least squares method, determine the parameters of the equation of the straight line described by equation (17)
- From equation (12) calculate the average molar mass of the tested polymer, assuming the following parameters: $K = 2{,}0\cdot10^{-2}$ cm^3/g and $c = 0{,}76$ determined for the poly-(vinyl alcohol) - water system at 25 °C.
- Based on the value of the Huggins coefficient (k') estimate the value range of the Flory interaction parameter (χ).