Viscosity determination of polymer solutions and gels by capillary and rotational viscometry

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 aqueous polyethylene glycol (PEG) solutions by capillary viscometer measurements and to calculate the molecular mass of the polymer. Also, to study the rheological behavior of carboxymethyl amylopectin (CMA) hydrogel by rotational viscometry and to learn the operation of rotational viscometer instruments.

1 Introduction

1.1 Macromolecular solutions and gels

Nowadays, the different polymers are widely used in many different applications (e.g. cosmetics and personal care products and they are essential components of drug delivery vehicles). Polymers are substances composed of macromolecules with molecular weights ranging from a few thousand to as high as millions of grams / mole. The IUPAC Gold Book definition of a macromolecule is: “A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.” Macromolecules can exist in practically unlimited number of conformations in their dissolved state. Linear polymers can be envisioned as chain-like molecules. These molecules are comprised of so-called segments – short sections of the macromolecule that move together thermally in solutions. Thus, polymeric molecules are not completely flexible; bending them requires energy. At the length scale below so-called persistence length (length of the segment), the polymer behaves more or less like a rigid rod. Often, the segments are simply the monomer units of the polymer chain, but the can be larger depending on many factors such as temperature.

Hydrogels are crosslinked polymeric networks, which have the ability to hold water within the spaces available among the polymeric chains. The hydrogels have been used extensively in various biomedical applications, viz. drug delivery, cell carriers and / or entrapment, wound management and tissue engineering. The water holding capacity of the hydrogels arise mainly due to the presence of hydrophilic groups, viz. amino, carboxyl and hydroxyl groups, in the polymer chains, it is dependent on the number of the hydrophilic groups and crosslinking density. Hydrogels can be classified into two groups depending on the nature of the crosslinking reaction. If the crosslinking reaction involves formation of covalent bonds, then the hydrogels are termed as permanent or chemical hydrogel. If the hydrogels are formed due to the physical interactions, viz. molecular entanglement, ionic interaction and hydrogen bonding, among the polymeric chains then the hydrogels are termed as physical hydrogels. The examples of physical hydrogels include polyvinyl alcohol – glycine hydrogels, gelatin gels and agar – agar gels. There are so-called stimuli responsive hydrogels, which change their equilibrium swelling with the change of the surrounding environment. E.g., the pH sensitive hydrogels have been used since long in the pharmaceutical industry. The swelling of hydrogels is characterized by the percentage swelling of the hydrogel, which is directly proportional to the amount of water imbibed within the hydrogel. Polyelectrolytes are macromolecular materials, which have multiple ionizable functional groups having different molecular weight and chemical compositions. When the ionizable groups dissociate, polymer molecules become charged either positively or negatively, depending upon the specific functional groups present. Polymers whose ionizable functional groups have a net positive charge are called cationic polyelectrolytes. Those with a net negative charge are referred to as anionic. Polyelectrolytes that bear both cationic and anionic repeat groups are called polyampholytes. The competition between the acid – base equilibria of these groups leads to additional complications in their physical behavior.

The CMA (carboximetil (-CH_2-COO-Na^+) amylopectin (Figure 1) is a branched chain polysaccharide, it is a gelatinizing material made of starch. The CMA, as a modified starch derivative is a typical anionic polymer, it swells in water and form hydrogel. Starch occurs in different plants, it is built up from different

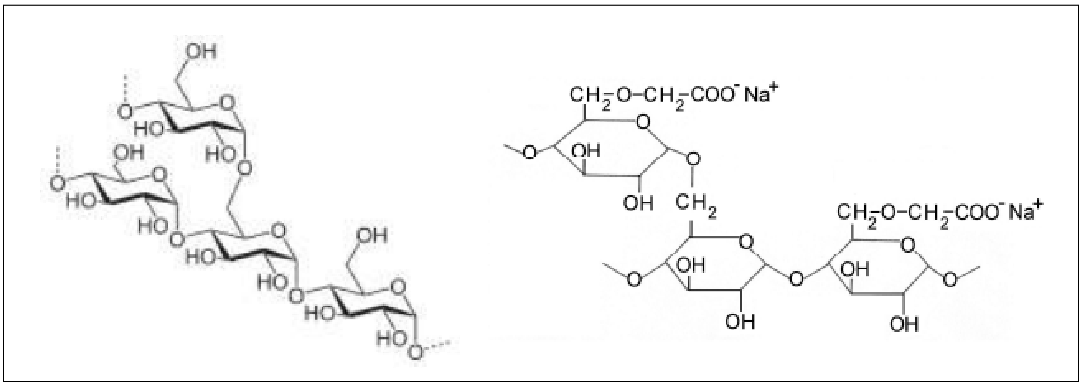

Figure 1: A part molecule structure of a branched chain polysaccharide (left side) and a carboximetil amylopectin (right side).

sugar molecules with chemical formula $(C_6H_{10}O_5)_n$. The number of monomers is between 10 and 500 thousands. Pure starch is a white, tasteless and odorless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Amylose is a much smaller molecule than amylopectin. About one quarter of the mass of starch granules in plants consist of amylose, although there are about 150 times more amylose than amylopectin molecules. It is synthesized by the alkali-catalyzed reaction of cellulose with chloroacetic acid.

The polar (organic acid) carboxyl groups render the cellulose soluble and chemically reactive. CMA is used in food as a viscosity modifier or thickener, and to stabilize emulsions in various products including ice cream. It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing, reusable heat packs, and various paper products. It is used primarily because it has high viscosity, is nontoxic, and is generally considered to be hypoallergenic as the major source fiber is either softwood pulp or cotton linter.

A polymer's properties and performance are influenced by its molecular weight and distribution. A high molecular weight, for example, can have an effect on both a polymer's brittleness as well as tensile strength. A low molecular weight can have an influence on a polymer's melt processing abilities. In general, polymers do not consist of assemblies of chains of constant length but rather a distribution of lengths, so that statistical techniques of analysis are needed to characterize them. The following methods are used for the determination of molecular mass of polymers:

- osmotic pressure
- light scattering
- ultracentrifugation and
- viscosity measurements.

1.2 Viscosity of the polymer solutions

The viscosity of the polymer solutions depends on the temperature, the solvent used, and the quality of the polymer, polymer molecular weight and concentration. According to the Einstein equation the relative viscosity (η_{rel}) of a suspension containing solid spheres depends only on the volume fraction of the particles (φ):

$$\eta_{\mathrm{rel}} = 2.5\varphi + 1\,,$$

where the relative viscosity ($\eta_{\mathrm{rel}} = \eta/\eta_0$) gives how many times the viscosity of the suspension (η) is greater than the viscosity of the solvent (η_0). The volume fraction of the polymer ($\varphi = \mathrm{v_p}/\mathrm{v_o}$) can be given by knowing the volume of the polymer ($\mathrm{v_p}$) in the solution with given volume ($\mathrm{v_o}$), this latter one can be calculated by knowing the mass (m) of the polymer dissolved in v_0 volume and the density (ρ_g) of the polymer coil:

$$\varphi = \frac{(\mathrm{m}/\rho_\mathrm{g})}{\mathrm{v_o}} = \frac{(\mathrm{m}/\mathrm{v_o})}{\rho_\mathrm{g}} = \frac{\mathrm{c_p}}{\rho_\mathrm{g}},$$

where c_p is the concentration of the polymer solution (g/ml). This latter expression is substituted into the Einstein equation we obtain the following equation

$$\eta_{\mathrm{rel}} = 1 + 2.5\frac{\mathrm{c_p}}{\rho_\mathrm{g}},$$

after rearrange the equation, we can get

$$\frac{\eta_{\mathrm{rel}} - 1}{\mathrm{c_p}} = \frac{2.5}{\rho_\mathrm{g}} = \frac{\eta_{\mathrm{sp}}}{\mathrm{c_p}},$$

where η_{sp} is the specific viscosity ($\eta_{sp} = (\eta - \eta_0)/\eta_0$). This equation is only valid for infinite diluted solution, where the interactions between flowing macromolecular coils are negligible, which can only be achieved by extrapolation for zero polymer concentration. By plotting the η_{sp}/c_p data as a function of the polymer concentration and extrapolating for zero polymer concentration, the so-called intrinsic viscosity ($[\eta]$) is obtaining:

$$\lim_{\mathrm{c_p}\to 0} \frac{\eta_{\mathrm{sp}}}{\mathrm{c_p}} = [\eta] = \frac{2.5}{\rho_\mathrm{g}}.$$

This correlation shows that the increase in viscosity during polymer dissolution is inversely proportional to the average polymer coil density (ρ_g). According to the KUHN – root law:

$$\rho_\mathrm{g} = \mathrm{K_p}\,\mathrm{M}^{-1/2}$$

the statistical coil density decreases with the increasing molecular weight (M). By combining the equations the obtained correlation is suitable for molecular weight determination:

$$[\eta] = \frac{2.5}{\mathrm{K_p}\,\mathrm{M}^{-1/2}} = \mathrm{K}_\eta\,\mathrm{M}^{1/2},$$

which is known as KUHN's viscosity law and it is valid for polymer solutions in theta – state (in which the expansion and contraction effects cancel each other and the polymer molecules in solution act like the ideal random coil) containing ideal statistical polymer coils.

In the case of real linear high polymers instead of ideal random coil, the situation is somewhat more complicated and the results is slightly different. The real long chains tend to form coils which are more extended than random ones, because of both the excluded volume effect and the usual interaction with the solvent. This tends to increase the apparent hydration and to increase the exponent. The relation between intrinsic viscosity and molecular mass can be expressed by the general equation proposed by KUHN–MARK–HOUWINK:

$$[\eta] = \mathrm{K}_\eta\,\mathrm{M}^{a},$$

where a and K_η are parameters characteristic for the specific polymer – solvent system and a is generally between 0.5 and about 0.85, and for any given solvent increases slightly with molecular mass. For many polymer / solvent couples they are tabulated in Polymer handbooks, some of them can be found in Table 1.

The relative viscosity of a polymer solutions can be measured by using a simple Ostwald viscometer by measuring the flow time. Since, according to the HAGEN–POISEUILLE law, the volumetric flow rate ($Q = V/t$):

$$\mathrm{Q} = \frac{\pi \cdot \mathrm{R}^4}{8 \cdot \mathrm{L} \cdot \eta} \cdot \Delta \mathrm{p}$$

depends on capillary geometry (R is the radius, L is the length), the hydrostatic pressure of the liquid column ($\Delta p \propto h\rho$, where ρ is the density of the liquid, h is the height of the column) and the viscosity (η) of the

Table 1: Constans for KUHN–MARK–HOUWINK equation.

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

flowing liquid. When the solvent and solution are tested in the same viscometer at the same flow volume, capillary geometry and liquid column height, than the viscosity is proportional to the product of the flow time requires for given volume (t for solution and t_0 for solvent flow time) and of density. If we disregard the difference in density between the solvent and the dilute solution ($\rho = \rho_0$), the relative viscosity can be written.

$$\eta_{\mathrm{rel}} = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \approx \frac{t}{t_0},$$

as a quotient of flow times. Thus, the specific viscosity of the dilute solution can be calculated with the following equation:

$$\eta_{\mathrm{sp}} = \frac{\eta-\eta_0}{\eta_0} \approx \frac{t-t_0}{t_0}$$

By measuring the flow time values of the solvent (t_0) and of different concentrations (c_p) solutions (t), the η_{sp}/c_p data can be calculated. If we plot these data as a function of c_p, the intrinsic viscosity $[\eta]$ can be determined (Figure 2).

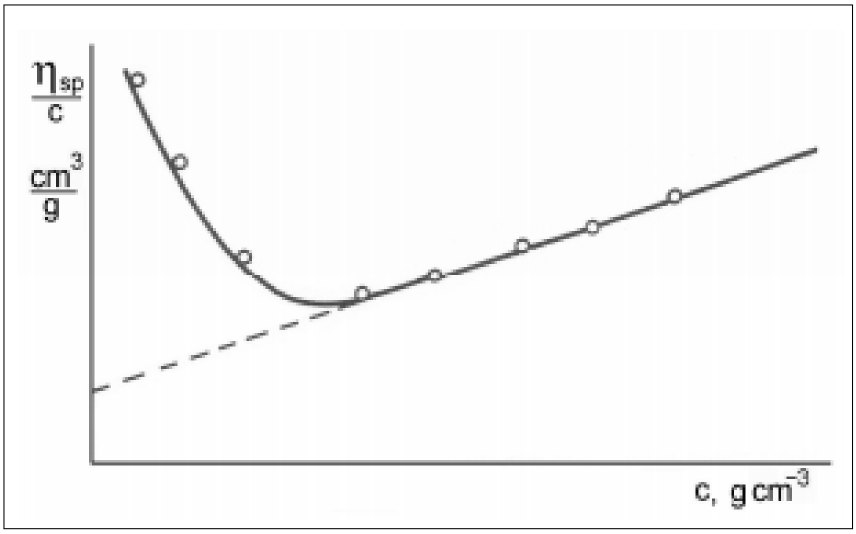

Figure 2: Determination of intrinsic viscosity $[\eta]$ by graphical extrapolation.

1.3 Rotational viscometry

The viscosity of the polymer solutions depends on the temperature, the solvent used, and the quality of the polymer, polymer molecular weight and concentration. The rotational viscometry is one of most appropriate tools to determine the viscosity of polymer solutions, gels, suspensions and other colloidal systems.

In rotary viscometers, the viscous medium being investigated is in the space between two coaxial bodies (cylinders, cones, spheres, or a combination of them); one of these bodies (the rotor) turns, and the other

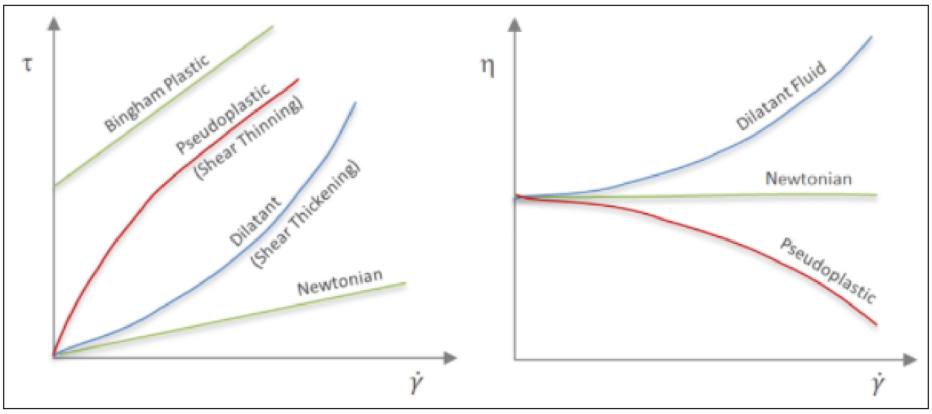

Figure 3: Viscosity-, and flow-curves of different reological systems.

is fixed. The viscosity is determined by the torque moment at a given angular velocity or by the angular velocity at a given torque moment. The rotation of the cylinder tangentially deforms the tested material, which resist against the deformation. Viscosity quantifies a material's resistance to flow. Fluids that move very easily, like water, have low viscosity, while thicker fluids such as paints with high solids content have much higher viscosity. Shear viscosity (η, N/m^2) is a function of shear rate, pressure, time and temperature and is mathematically defined as shear stress (τ) divided by shear rate (γ):

$$\eta = \frac{\tau}{\gamma},$$

or after rearrange the equation:

$$\tau = \eta \gamma .$$

Shear stress is a measure of the force acting on a cross-section of a material sample in a direction parallel to its plane. The application of shear stress induces deformation in a sample; shear strain quantifies the degree of deformation. Shear rate is the rate of strain change over time. A material that exhibits viscosity that is independent of shear rate is known as Newtonian, and a single viscosity measurement is needed to define its behavior. Newtonian behavior, where the the shear stress (τ) is a linear function of the shear rate (γ), i.e. the viscosity (η) is constant, is common for pure, small-molecule fluids and very dilute dispersions. More complex materials – such as polymer solutions, suspensions and emulsions – tend to exhibit non-Newtonian behavior, that is, either viscosity decreases (shear thinning) or, less commonly, viscosity increases (shear thickening) with increasing shear rate (see Figure 3). This occurs as a result of the material's complex microstructure and the way it rearranges under the applied stress, and can be beneficial for many products. Therefore, the flow properties of these materials cannot be described by a single slope (η), but the flow-curves $\tau = \mathrm{f}(\gamma)$, or viscosity curves $\eta = \mathrm{f}(\gamma)$ are used for their characterization (Figure 3).

In the case of flow curves of plastic (Bingham plastic fluids) or pseudo – plastic systems, the slope of the curve provides the plastic viscosity (η_{pl}), while by the extrapolation of the linear section to $\gamma = 0$, the BINGHAM yield strength (τ_{B}) can be determined (Figure 3):

$$\tau = \tau_{\mathrm{B}} + \eta_{\mathrm{pl}} \mathrm{D} .$$

There are systems (pastes, creams, gels) whose viscosities depend on the magnitude of the mechanical action applied and the time of action. This behavior can be measured and characterized if the relaxation time of the systems ($10 - 10^3$ s) is comparable to the measurement time.

The most common time-dependent phenomena are: *(1)* Thixotropy, when a shape-retaining, solid-like structure that builds up over a longer or shorter period of time, collapses under mechanical stress (e.g. shear), and becomes liquid; then thereafter the structure of the fluid-like system builds up again during rest time. This isothermal, reversible sol – gel transformation can be characterized by the thixotropic loop (Figure 4).

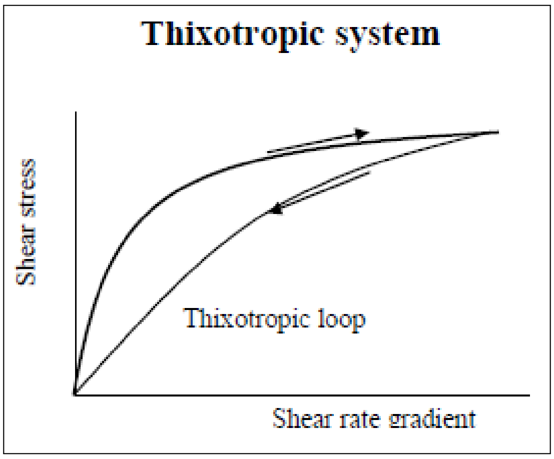

Figure 4: Flow-curve of a typical thixotropic system with the hysteresis loop.

(2) The opposite of this is the antitixotropy or negative thixotropy. *(3)* Rheopecty or rheopexy is the phenomenon where the structure builds up during slow mixing. Rotary viscometers are suitable for studying these phenomena.

Rotational viscometers are used to measure viscosity. Rotational viscometers work by getting the measurements of the torque on a vertical stand that moves the spindle in a rotational direction. The rotation of the spindle is usually proportional to how viscous the sample is. The spindle is driven at a constant angular velocity by a motor through a torsion wire and the outer cylinder is fixed. The shear strain (τ) is proportional to the motor rotational speed, because:

$$\tau = \frac{\mathrm{du}}{\mathrm{db}} \approx \frac{\Delta \mathrm{u}}{\Delta \mathrm{b}} = \mathrm{k\,r\,\omega} = 2\mathrm{k}\pi\mathrm{n}, \quad \text{where}$$

Δb: the gap,

Δu: the circumferential speed of the inner cylinder,

r: the radius of the inner cylinder,

ω: angular velocity of the inner cylinder,

n: the speed of the inner cylinder,

k: constant

The spindle, when inserted into the test liquid, rotates at various fixed speeds, thereby shearing the material continuously at defined shear rates. Simultaneously the viscometer measures the amount of torque resistance experienced by the spindle at each speed of rotation. This torque measurement is quantified as a “shear stress”, which acts across the surface area of the immersed portion of the spindle.

2 The goal of the exercise and experimental work

2.1 Determination of polymer molecular mass by capillary viscosity measurements

The purpose of the measurement is to determine the intrinsic viscosity [η] of polyethylene glycol (PEG) polymer solution and to give the molecular weight of the polymer.

Tools and equipments: Ostwald viscometer, stop-watch, 50 ml volumetric flask, 25 ml volumetric pipette, 10 ml volumetric pipette, 5 pieces of 50 ml beaker, balance (accuracy 0.01 g).

Materials: polymer: PEG (polyethylene glycol), samples of different molar masses, solvent: distilled water.

Prepare PEG stock solution by measuring a given amount between 3.5 – 7.5 g PEG and dissolve it into a 50 ml volumetric flask. *Unless the instructor says otherwise*, the amount of polymer to be measured should be 5 g. *Important: Polymers can dissolve slowly in good solvent only. Their dissolution starts with swelling. Observe the swelling of solid PEG pieces. Remove the air bubbles adhered on solid phase by gentle rotation. Do not shake the flask before filling up to the meniscus! PEG solution foams strongly*. Make dilution series by repeated double dilution of stock solution in such a way that remove 25 ml of stock solution from 50 ml volumetric flask into a 50 ml beaker, then dilute the remaining 25 ml by distilled water, homogenize it and take out 25 ml of dilute solution and pour into another 50 ml beaker. Repeat this dilution process twice more. Before measuring, wash the viscometer thoroughly with distilled water. Measure the viscosity of aqueous solutions with capillary viscometer. Pipette 10 ml of water first and measure the flow time of water three times, then that of the solutions with increasing concentration, each three times. The dilute aqueous solutions of PEG (polyethylene glycol) are Newtonian liquids, their viscosity does not depend on the flow rate, it is constant at a given concentration and constant temperature.

2.2 Determination of hydrogel viscosity by rotational viscometry

The aim of exercise is to show the effect of CMA on the structure formation in CMA gels and their rheological behaviour. During practice, the task is to prepare a hydrogel sample with a defined viscosity value by adjusting the concentration of the polymer. To achieve this, first we determine the viscosity of the available 5 %w/v CMC gel. Next a two-fold dilution of the polymer is prepared and its viscosity is also determined.

Next, in the light of the viscosity results thus obtained, prepare a sample having a viscosity value between the 5 and 2.5 %w/v CMC gel. Unless the instructor says otherwise, the viscosity of the gel should be 25 % of the starting 5 %w/v CMC polymer gel. The other aim of the exercise is to determine in what type of rheological system the studied aqueous CMC gel belongs to and to explain its rheological behavior. For this, we measure the evolution of the polymer gel viscosity under continuously increasing rotation speed.

Tools and equipments: ST-2020L rotary viscometer with four spindles (L1 – L4), glass cylinder, 5 pieces of 100 cm^3 beaker, 4 pieces of glass sticks, 10 ml volumetric pipette.

Materials: 5 % CMC hydrogel, distilled water.

1. First, the rotary viscometer must be install according to the attached user manual.
2. Next the viscosity of the available 5 %w/v CMC gel must be determined according to the measurement instruction. The results obtained are summarized in the table below[1]:

x% polymer concentration; T= °C			
rotational speed (rpm)	range (%)	spindle	viscosity (mPa s)

3. Investigate how the initial (5 %) CMC polymer gel behaves under increasing shear forces. For this, the viscosity of the gel is measured under increasing rotational speeds. During the measurement, the shear values used must be chosen so that the measured viscosity values vary by at least one order of magnitude. In this case, it is not necessary to aim for the percentage of the measuring range to be close to 100 %.
4. By knowing the viscosity of the 5 % CMC gel, prepare a two-fold serial dilution sample with distilled water and determine its viscosity as described in previous point. After the addition of the distilled water the homogenization of the sample can be facilitated by mixing using a glass stick.

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[1] It is a common mistake for students to record only the final rotational speed and viscosity values, but the table should include the viscosity values for all speeds, i.e., what speed values were chosen to determine the exact viscosity value of the sample during the measurement.

5. Finally, by knowing the concentration dependence of the viscosity values, prepare a gel whose viscosity is given by the instructor. Unless the instructor says otherwise, the viscosity of this gel should be 25 % of initial (5 %w/v) sample.

3 Evaluation of the results

3.1 Determination of polymer molecular mass by capillary viscosity measurements

1. Calculate the relative and specific viscosities of the solutions and tabulate the results:

PEG solution		flow time, s				$\eta_{rel} = t/t_0$	$\eta_{rel} - 1 = \eta_{spec}$	η_{spec}/c_p
Dilution	c_p g/ml	1.	2.	3.	average			
∞ (water)	0					1	0	-

2. Plot the η_{spec}/c values as a function of c to determine the intrinsic viscosity $[\eta]$ (see Figure 2), finally calculate the molecular weight by using Mark and Houwink equation and constants van be found in Table 1. Interpret the results in a few sentences.

3.2 Determination of hydrogel viscosity by rotational viscometry

1. Summarize the results of viscometric measurements in tabular form.
2. Plot the measured viscosity values as a function of the polymer concentration and interpret their evolution.
3. Investigate how the viscosity of the CMC polymer gel changes with increasing shear forces. After plotting the viscosity curve, evaluate the flow character of CMA gels.

Control questions

1. Write the most important properties of macromolecular solutions!
2. What is theta-state?
3. Which properties of macromolecular solutions are suitable for determination of molecular mass?
4. What kind of viscosity is characteristic of macromolecules dissolved in a solvent? Is it related to the molecular weight?
5. How can you measure the relative viscosity of a solution?
6. How can you determine the intrinsic viscosity of macromolecular solution from the measured viscosity data?
7. What are hydrogels? Classify them into two groups depending on the nature of the crosslinking reaction!
8. What is rheology? What is flow curve?
9. List the basic deviations from Newtonian behaviour of liquids!
10. Explain the shear thinning flow behaviour!
11. What is the thixotropy?
12. Draw the flow and viscosity curves of a pseudoplastic system!
13. What is CMA?