

Viscometry of polymer solutions

Literature: P.W. Atkins: *Physical Chemistry*, Chapters 26.1–3 (4th edition), or 25.1–3 (6th edition).

Type of practice: Individual.

Aim of the practice: The goal of the exercise is to study the viscosity of aqueous polymer solution by Ostwald capillary viscometer and to calculate the conformational properties of the polymer from the viscosity data obtained.

1 Introduction

1.1 The ideal and real random coil

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 segments¹ – 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 they can be larger depending on many factors such as temperature. This practice shows a way to obtain information on the size features of polymer molecules by measuring their viscosities in solvent series, because the viscosity of polymer solutions are highly dependent on the conformational states of dissolved macromolecules, and is therefore a very sensitive tool to detect the related structural changes. An ideal chain (or freely-jointed chain) is the simplest model to describe polymers. It only assumes a polymer as a random walk (comparing the shape of molecule to the pathway of an object that moves in random steps in space) and neglects any kind of interactions among monomers. In this model, segments are rigid rods of a fixed length (l), and their orientation is completely independent of the orientations and positions of neighboring monomers, to the extent that two monomers can co-exist at the same place.

The most straightforward way to study the size and shape features of the macromolecule is to model the statistical properties of the random coil, as this is the most probable shape of the long-chain polymer. The coiled state of the macromolecule chains was first recognized by W. Kuhn (1934). Theory says that the mean length of the coiled ideal chain, that is, the statistical end-to-end distance ($\langle h^2 \rangle_0^{1/2}$) reads:

$$\langle h^2 \rangle_0 = n \times l^2, \text{ or } \langle h^2 \rangle_0^{1/2} = l \times n^{1/2}, \quad (1)$$

where n is the statistical segment number, while l is the statistical segment length. Since the n segment number is proportional to the molecular weight (M), Kuhn's root law applies:

$$\langle h^2 \rangle_0^{1/2} = \text{const} \times M^{1/2}. \quad (2)$$

Although the ideal random coil model is a good model for the description of the behavior of dissolved polymer chains, in real systems the conformational properties of the macromolecules are different because they are affected by several factors. Excluded volume causes the ends of a polymer chain in a solution to be further apart (on average) than they would be were there no excluded volume (in case of ideal chain model). Temperature and solvent composition are typical parameters that tune the conformation of real macromolecular coils by the variation in the segment-segment (e.g. intramolecular van der Waals attraction) and segment-solvent (solvation) interactions.

The attraction between polymer segments would lead to contraction of the molecule, while the solvation would induce full expansion of the molecule. In so-called good solvents (usually solvent mixtures), the latter

¹A segment of an actual polymer chain which behaves, with respect to some property, virtually as a segment of a freely jointed chain.

dominates, giving rise to larger statistical end-to-end distances than that of the corresponding ideal chain of the same molecular composition and weight. These expanded molecules are then gradually contracted upon the addition of a solvent of poorly solvating ability. Reaching a certain composition, the polymer molecules reach the so-called theta state, in which the expansion and contraction effects cancel each other and the molecules in solution act like the ideal random coil. The solvent in which this happens is termed as the theta solvent, and it is usually a binary mixture of two liquids, one of which dissolved the polymer well, and the other does not. According to Flory (the theoretician who contributed well to the establishment of physical chemistry of polymer solutions), the “coil-out” can be expressed as the α expansion factor:

$$\langle h^2 \rangle = \langle h^2 \rangle_0 \times \alpha^2, \quad (3)$$

where $\langle h^2 \rangle_0$ is the statistical end-to-end distance in real solvent condition. $\langle h^2 \rangle_0$ can be determined experimentally only in Θ -condition, where $\alpha = 1$. Under laboratory conditions, the Θ -temperature can only be set for some solvent–polymer systems, therefore, the Θ -state of a polymer at given temperature can be achieved in a solvent/precipitant binary mixture system. Thus, by gradually adding the precipitant to the polymer solution (in good solvent), the Θ -condition can be achieved at a given temperature, i.e. when the expansion and contraction effects cancel each other. Exceeding the theta-state, the macromolecules precipitate depending on their molecular weight and phase separation takes place due to the strong associative polymer–polymer interaction.

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):

$$\eta_{rel} = 1 + 2.5 \times \phi, \quad (4)$$

where the relative viscosity ($\eta_{rel} = \eta/\eta_0$) 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 ($\phi = V_P/V_0$) can be given by knowing the volume of the polymer (V_P) in the solution with given volume (V_0), 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:

$$\phi = \left(\frac{m}{\rho_g} \right) \times V^{-1} = \frac{c}{\rho_g}, \quad (5)$$

where c is the concentration of the polymer solution (g/ml). This latter expression is substituted into the Einstein equation (4) we obtain the Eq. (6)

$$\eta_{rel} = 1 + 2.5 \times \frac{c}{\rho_g}, \quad (6)$$

after rearrange the equation, we can get

$$\frac{(\eta_{rel} - 1)}{c} = \frac{2,5}{\rho_g} = \frac{\eta_{sp}}{c}, \quad (7)$$

where η_{sp} is the specific viscosity ($\eta_{sp} = (\eta - \eta_0)/\eta_0$).

The Eq. (7) 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 data as a function of the polymer concentration and extrapolating for zero polymer concentration, the so-called intrinsic viscosity ($[\eta]$) is obtaining:

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = [\eta] = \frac{2.5}{\rho_g}. \quad (8)$$

The (8) 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:

$$\rho_g = K_\rho \times M^{-1/2}. \quad (9)$$

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

$$[\eta] = \frac{2.5}{K'_\eta} \times M^{-1/2} = K'_\eta \times M^{1/2}, \quad (10)$$

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 molecular weight 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:

$$[\eta] = K_\eta \times M^a, \quad (11)$$

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 handbooks², some of them can be found in Table 1.

Since, according to the HAGEN – POISEUILLE law, 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. Thus, we can describe:

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta - \eta_0}{\eta_0} = \frac{t \times \rho - t_0 \times \rho_0}{t_0 \times \rho_0} \approx \frac{t - t_0}{t_0}. \quad (12)$$

Since the density of the solution and the solvent differ only slightly ($\rho = \rho_0$), it is sufficient to measure the t flow times at different concentrations. By measuring the flow time values of the solvent (t_0) and of different concentrations (c) solutions (t), the data can be calculated. If we plot these data as a function of c , the intrinsic viscosity $[\eta]$ can be determined (Fig. 1.). The slope of the η_{sp}/c curve can often be described by the empirical Huggins equation (13).

$$\frac{\eta_{sp}}{c} = [\eta] + K_H \times [\eta]^2 \times c. \quad (13)$$

In the second term of the Eq. (13), the $K_H \times [\eta]^2$ coefficient is characteristic of the goodness of the solvent, i.e. of the degree of strength of the solvent – polymer interaction.

Eq. (13) is analogous to the $B/c = RT/M + Bc$ relation known from the osmometry, where the second virial coefficient (B) is also characteristic for the solvation and thus, related to the Huggins coefficient can be calculated from the viscosity measurement.

1.3 Calculation of conformational parameters from viscosity data

Based on the experimental findings the properties of the polymer solutions are primarily determined by the weight, size and shape of the macromolecule chains. The conformational properties (e.g. shape and size)

²<http://search.ebscohost.com/login.aspx?direct=true&scope=site&db=nlebk&db=nlabk&AN=196653>

Table 1: Constants for Kuhn – Mark – Houwink equation.

Polymer	Solvent	T (°C)	$K_{\eta}(10^{-2})(\text{mL/g})$	a
Polyethylene	Xylene	75	1.35	0.74
Polyisobutylene	Benzene	24	8.30	0.50
Polystyrene	Benzene	25	1.03	0.74
Polystyrene	Toluene	30	1.20	0.72
PMMA	Methyl ethyl ketone	25	0.58	0.72
PMMA	Chloroform	25	0.34	0.83
PVA	Water	25	4.28	0.64
PVA	30/70 V/V% n-PrOH-water mixture	25	2.10	0.74
Epoxy resin	Dioxane	25	3.98	0.61

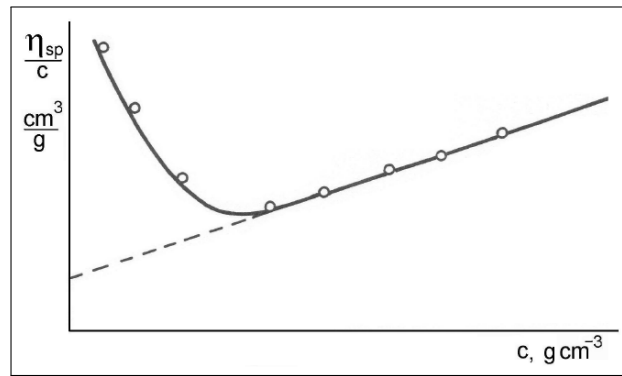


Figure 1: Determination of intrinsic viscosity $[\eta]$ by graphical extrapolation³.

of a dissolved polymer molecule are determined by the thermodynamic conditions and chemical structure. Hence, the statistical size of the macromolecule can be determined using two factors. One is the „goodness” of the solvent, which affects the size of the polymer coils through the solvation. The other is the structural structure of the polymer chain itself. Thus, depending on the structure of the macromolecule and the nature of the solvent, the conformational properties of the polymer molecule can be different.

The general correlation between the intrinsic viscosity, the relative molecular weight and the size of the molecule, according to Kirkwood and Riseman is as follows:

$$[\eta] = \frac{\Phi \times \langle h^2 \rangle^{3/2}}{M}, \quad (14)$$

where $\langle h^2 \rangle^{1/2}$ is the statistical end-to-end distance in real solvent condition and Φ is a constant. Using Flory’s equation (3), this is reformulated as

$$[\eta] = \frac{\Phi \times \langle h^2 \rangle_0^{3/2} \times \alpha^3}{M}, \quad (15)$$

where α is the Flory-expansion factor and $\langle h^2 \rangle_0^{1/2}$ is the end-to-end distance in theta state. Since in

³The possible “abnormal” bending of the curve at low polymer concentrations is caused by the adsorption of the polymer on the capillary wall. This causes a large difference, especially at lower concentrations, where the difference in viscosity and thus in flow time is small between the polymer solution and the pure solvent.

theta-state (the ideal situation) the expansion factor is 1, Eq. (16) and (17) can be written as:

$$[\eta]_{\Theta} = \frac{\Phi \times \langle h^2 \rangle_0^{3/2}}{M}, \quad \text{and} \quad (16)$$

$$\frac{[\eta]}{[\eta]_{\Theta}} = \alpha^3. \quad (17)$$

Thus, if the intrinsic viscosity is determined in theta-state, the expansion factor characteristic for the given solvent can be determined. According to literature, the value of the Φ constant is $2.87 \times 10^{23} \text{ g}^{-1}$. With this, the values of statistical end-to-end distances (mean chain lengths) can be calculated using Eq. (14) and (16). These data give important information on the solution state of the polymer molecule.

1.4 Poly(vinyl alcohol) (PVA)

Due to its structure, polyvinyl alcohol is a highly water-soluble (hydrophilic) synthetic polymer that produced industrially by alkaline hydrolysis of polyvinyl acetate (PVAc) (Fig. 2). The degree of hydrolysis significantly affects the properties of the polymer produced: while the fully hydrolysed PVA is highly soluble in cold water as well, but as the degree of hydrolysis decreases, the water solubility of the macromolecule decreases significantly. Polyvinyl alcohol has excellent film-forming, emulsifying and adhesive properties. Due to its advantageous behaviors, it is widely used in the packaging industry, agriculture, textile and paper industry, as well as as a raw material for adhesives, but due to its biocompatible properties, the pharmaceutical industry also uses significant quantities.

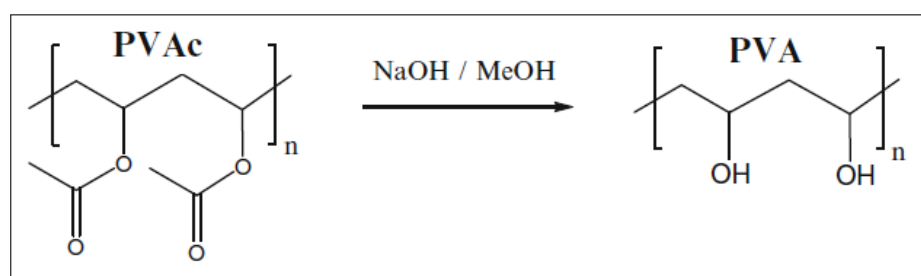


Figure 2: Synthesis of PVA from PVAc.

2 Experimental work

- During the exercise the conformational properties of PVA polymer will be determined in good (30 v/v% n-propanol + 70 v/v% distilled water) and in theta (45 v/v% n-propanol + 55 v/v% distilled water) solvents by viscometry measurement.
- To do this, prepare 30–30 mL of 5 % PVA solutions both in good and in theta solvents from the available 10 % (10 g/100 mL) PVA aqueous stock solution. During the dilution, first, water should be added to the calculated volume of the polymer stock solution, then, after homogenization, the propanol and the obtained solution must be mixed thoroughly. *It should also take into account the water content of the PVA stock solution during the preparation of the samples.*
- In addition to PVA containing polymer solutions, 50–50 mL of propanol / water binary mixtures of the same composition must be also prepared for the measurements.

Table 2: Summary of experimental results.

$V_{\text{PVA solution}}$ (mL)	c_{PVA} (g/mL)	flow time (s)	η_{sp}	η_{sp}/c (mL/g)	ρ_{g} (g/mL)
0		$t_{0,\text{average}} =$	–	–	–
0.5					
1...					

- After preparation of the solutions and pure solvents mixture, the viscosity of the polymer solutions with increasing PVA concentrations should be determined with the Ostwald capillary viscometers⁴. Separate viscometers are used for the two different solvents based samples, the viscometer with the shorter flow time is selected to measure the theta solvent.
- Before starting the measurements, pour out the water from the capillary viscometers and wash the devices twice with 2-3 mL of pure solvent mixtures, and then, remove the solvent carefully – preferably without residue – from the viscometer tube.
- Then, 10 mL of the pure solvent mixture pipette into the viscometers, and the liquid draw up so that the liquid level reached above the upper mark on the thinner stem of the device. The flow times between the two marks (thus, belonging to the same volumes) are then measured (t_0). The measurement is repeated at least once again, in case of too large ($>2-3$ s) deviation, twice.
- During the flow time measurements of PVA the solutions, 15 mL of the pure propanol / water mixture was pipetted into a beaker, then 0.5 mL of PVA solution from the sample with the same mixture composition was added and the obtained solution was thoroughly homogenized. Next, the flow time of the sample (t_1) is determined using 10 mL of this solution. After the measurement, the solution is poured back completely into the beaker making sure that no liquid remains in the device.
- After adding additional 0.5 mL volumes of polymer solution, the measurements are repeated so many times that we have at least 10–10 measuring points for both the good and theta solvents. The measurements are performed parallel with the two mixtures using both viscometer.
- After completing the measurements, wash the viscometers at least three times with distilled water and then fill them with water.

3 Evaluation of the results

- Table 2 should be prepared for both series based on the volumes used in the preparation of solutions, The specific viscosities (η_{sp}) and coil density values (ρ_{g}) can be calculated according to the Eq. (12) and (6), respectively, where $\eta_{\text{rel}} = t/t_0$.
- Next, plot the $\eta_{\text{sp}}/c = f(c)$ functions for both series and the intrinsic viscosity values ($[\eta]$ and $[\eta]_{\Theta}$) are also determined according to the Fig. 1 and Eq. (13).
- The relative molecular weight (M) of the polymer can be calculated by the Kuhn–Mark–Houwink equation. Eq. (11) using the intrinsic viscosity value ($[\eta]$) obtained for the „good solvent”, then the square root of the root mean square end-end distance ($\langle h^2 \rangle^{1/2}$) according to the Eq. (14).

⁴It is a special, U-shaped glass tube. In one arm of the U is a vertical section of a narrow capillary. Above that there is a bulb, with it is another bulb lower down on the other arm. In use, liquid is drawn into the upper bulb by suction, then allowed to flow down through the capillary into the lower bulb. Two marks (one above and one below the upper bulb) indicate a known volume. The time taken for the level of the liquid to pass between these marks is proportional to the kinematic viscosity, and if the densities do not differ much, it is also proportional with the dynamic viscosity.

- For both series, plot the coil density values (ρ_g) as a function of polymer concentration and explain the evolution of the values.
- Finally, the value of the Flory expansion factor (α) is also calculated according to the Eq. (17).
- Evaluate the results and the acceptability of the obtained data in a few sentences.
- Knowing the molecular weight (M) of the polymer and the molecular weight (M_0) of the repeating vinyl alcohol units, give the estimated degree of polymerization of the PVA polymer ($P = M/M_0$), i.e. the number of repeating units in the macromolecular chain.
- Knowing the degree of polymerization and the bond length of the C-C bond (0.154 nm) as well as assuming a bond angle of 110° , calculate the average theoretical length of the PVA chain molecules. Compare this value with the calculated size of the polymer coil.

Control questions

1. What does the viscosity of the polymer solutions depend on?
2. What conformational parameters can be determined from viscosity measurements?
3. Note down and interpret the Kuhn's root law.
4. Note down and interpret the Kuhn's viscosity law.
5. Note down and interpret the Kuhn – Mark – Houwink law.
6. Note down and interpret the Huggins law.
7. How can you determine the α expansion factor from the measured viscosity data?
8. What parameters affect the size of a macromolecular coil?
9. How can you determine the statistical end-to-end distance from the measured viscosity data?
10. Why only the so-called $[\eta]$ intrinsic viscosity can be used to determine viscosimetric molecular weight?