KEMS448 Physical Chemistry Advanced Laboratory Work

Viscosity: Determining the Molecular Mass of Polyvinyl Alcohol

1 Introduction

The internal friction in fluids, or viscosity, is caused by the cohesion forces between molecules. Molecules need energy to escape from each others' close interactions. Viscosity is therefore a thermodynamic quantity, dependent on temperature and pressure. The viscosity of a polymeric solution is, in addition, a colligative property dependent on the concentration and molecular weight of the polymer in the solution.

The dependence of polymeric solution's viscosity on the molecular mass can be used to determine the molecular mass of the polymer, an important parameter when characterizing polymers and their properties. In this laboratory work, the concept of viscosity is introduced, and the dependence of viscosity of polymeric solutions on their concentration and molecular mass is examined. The molecular mass of the polymer in the solution is determined using an Ostwald viscometer.

2 General facts about viscosity

Viscosity can be said to describe the resistance of a fluid to flow. Viscosity is characteristic to the fluid in question, and is used to define the qualities of, say, oils, resins, latex paints or even chocolate pudding. Viscosity is one of the so called flux quantities, because it affects mass transfer, or in other words, diffusion in a medium. Thus, it affects for example the reaction kinetics in solutions.

Macroscopically, viscosity is a friction force quantity caused by molecules' directional movements past each other in a fluid. Microscopically, viscosity depicts the energetics associated with molecular interactions. To make a fluid flow, energy must be brought into the system, so that the attractive forces between molecules are surpassed. These attractive forces influence, for example, the vaporization enthalpy and surface tension.

2.1 Newtonian fluid viscosity

Let us assume the fluid to be flowing evenly into a direction x, as in figure 1. Additionally, assume the fluid to be composed of plates such as in the picture, both with surface area A. The plates are moving tangentially to their surface into positive or negative x direction.

In 1678 Isaac Newton published a rule for a simple shear flow: "the resistance caused by the lack of slippiness between parts of the liquid is directly proportional to the velocity at which the parts of the liquid are separating from each
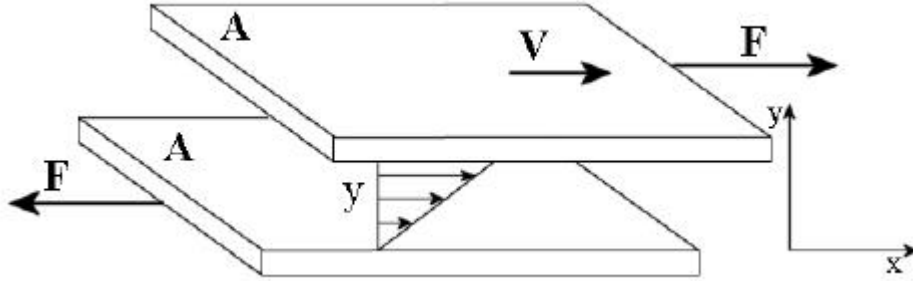
Figure 1: *According to Newton's postulate, the force F caused by the movement of the upper plate per area A is directly proportional to the velocity gradient V/y=cut velocity. The proportionality coefficient is called the Newtonian viscosity or dynamic viscosity μ (see equations 3 and 4).*

other." This "lack of slippiness" is now called dynamic viscosity, or the viscosity coefficient. The coefficient can be defined by examining a flow between two collinear plates (figure 1).

When the upper plate experiences a tangential force F, the plate begins to move at a constant velocity v. Thus the fluid is being sheared and it starts to move at a shear velocity inversely proportional to the viscosity of the fluid. To keep the movement constant, a force F must be directed at the plate, and its value per unit area is called the shear stress, σ:

$$\sigma = \frac{F}{A},\tag{1}$$

where A is the surface area of the plate. The units for σ, $[\sigma] = \frac{N}{m^2} \equiv Pa$ are used. The velocity gradient, with which fluid layers like in figure 1 are moving, is called the shear velocity $\dot{\gamma}$. Infinitesimally

$$\dot{\gamma} = \frac{dv}{dy},\tag{2}$$

where dv is the difference in velocity between the plates or layers of fluid and dy the distance between the plates. According to Newton's postulate, the viscosity coefficient η is the ratio of shear stress and shear velocity needed for a constant velocity of a plate.

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$$\eta = \frac{\sigma}{\dot{\gamma}}, \tag{3}$$

where σ and $\dot{\gamma}$ are the same quantities as before and $[\eta] = \frac{Pa}{s^{-1}} = Pa \cdot s$. Typically all fluids with small enough molecules behave according to Newtonian fluid mechanics. Newtonian fluids are for example water and glycerol. According to equation 3, the Newtonian shear stress can be written as
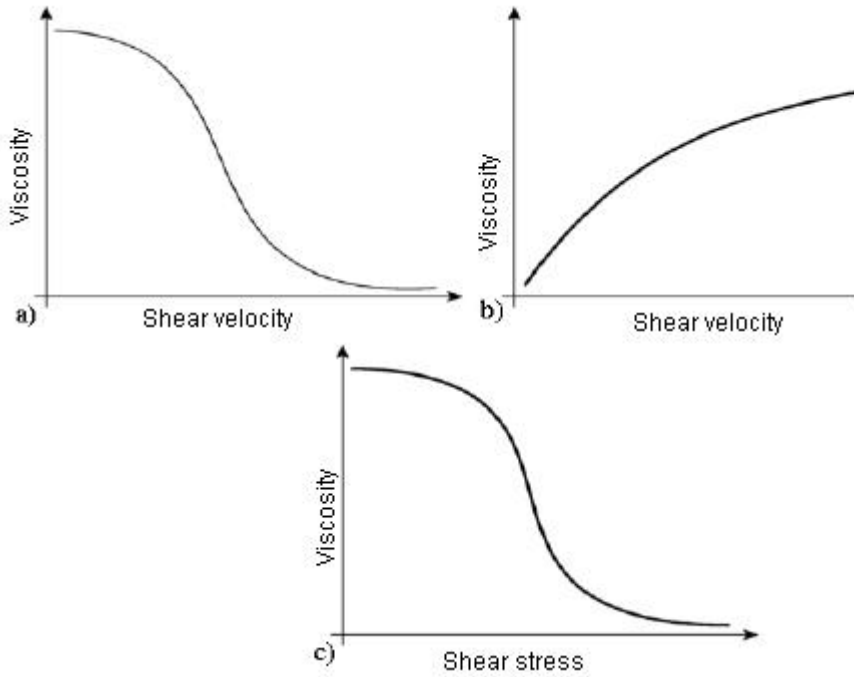
$$\sigma = \eta \frac{dv}{dy}. \tag{4}$$

Figure 2: *A pseudoplastical polymeric solution's a) viscosity against shear velocity, b) shear stress against shear velocity, c) viscosity against shear stress.*

2.2 Non-Newtonian fluid viscosity

A great number of fluids do not obey Newton's fluid mechanics (equation 4). Fluids with nonlinear viscosity coefficients are called non-Newtonian fluids. Non-Newtonian viscosity is a function of temperature and pressure, and also shear velocity or time.

Non-Newtonian behaviour can be commonly observed for polymeric solutions and fluids. The viscosity of a very dilute polymeric solution in a Newtonian fluid is Newtonian, and therefore constant. On the other hand, Newtonian behaviour has been observed also for larger polymeric molecules with shear stresses under $0.01 \frac{N}{m^2}$.

Generally, liquid polymers, polymeric solutions and many colloidal systems behave pseudoplastically, or "shear-thinningly" and their viscosities decrease as the shear velocity is increased. Pseudoplastical liquids have a typical behaviour of their viscosity changing as a function of the shear velocity, which can be observed from the graph in figure 2a).

From the viscosity graph in figure 2a), it can be seen that at very small and at very large shear velocities, viscosity stays nearly constant. These two regions are called the first and second Newtonian regions of a pseudoplastical liquid. Experimentally, these two regions are almost always very hard to achieve and most commercial viscometers can only detect the region of exponential dependence between them. In addition to shear-thinning, also elastic thickening and thinning can be observed for polymeric solutions, and other viscoelastic phenomena, which all make it more difficult to determine molecular masses for polymeric systems.

2.3 Viscosity's dependence on concentration and molecular mass

In a polymeric solution, the viscosity grows as either concentration or molecular mass increases. In an infinitely dilute solution, the viscosity nears the solvent's viscosity η_s

$$\eta = \eta_s(1 + [\eta]c + k_1[\eta]^2c^2 + \ldots). \tag{5}$$

The coefficient $[\eta]$ is called the limiting viscosity and

$$[\eta] = \lim_{c \to 0} \left(\frac{\frac{\eta}{\eta_s} - 1}{c} \right), \tag{6}$$

where the denominator

$$\frac{\eta}{\eta_s} - 1 \equiv n_{sp} = \frac{Cv}{V} \tag{7}$$

is the specific viscosity. According to equation 7, the specific viscosity n_{sp} is proportional to the ratio of the velocity of the dissolved polymer v and the velocity

of the solvent V. Thus n_{sp} is a colligative property that depends on the amount of the dissolved polymer. In equation 7, C is a parameter depending of the polymer's geometric form, which for spherical objects gets the value $\frac{5}{2}$.

Flory and Fox proposed in 1951 that for an extremely diluted polymeric solution, the limiting viscosity is proportional to the third power of the polymer radius of inertia and inversely proportional to the molecular mass, which gives for the total molecular mass dependence, ideally, $[\eta] \propto \sqrt{M}$. Flory and Fox also assumed the hydrodynamic effects of the polymer's spatial coordinates to equal those of a spherical empty shell. The Flory-Fox model has later been replaced with the so-called Mark-Houwink model, in which the mean molecular mass of the polymers, $\overline{M}$ can be determined from the limiting viscosity by

$$[\eta] = K\overline{M}^a, \tag{8}$$

where K and a are parameters dependent of the polymer, solvent, and the temperature. The parameter a depends on the polymer's conformation and ideally $a \approx 0.5$. Typically, for polymer-solvent-pairs, a varies between values of 0.5 and 1.0, and K between 10^{-4} and 10^{-7} (see table 1). The empiric equation 8 is usually called the Mark-Houwink or Mark-Houwink-Sakurada equation. For styrofoam-N-buthyl benzene, the behaviour of the solution's viscosity depending on the polymer concentration can be seen in figure 3a). The shear thinning behaviour can be seen from the figure: viscosity decreases as the shear velocity is increased. An example of determining the limiting velocity can be seen in figure 3b). The polymer's molecular mass can be determined from the Mark-Houwink equation when the parameters a and K are known. Some known parameters are given in table 1.

2.4 Polymers

One of the important characteristic parameters of polymers is their molecular mass. Many physical properties can be explained through the mass or shape distribution curve. By measuring the limiting viscosity, the molecular mass or the hydrodynamic radius of inertia can be determined. The polymer used in this laboratory work, polyvinyl chloride, is linear, which means that the macromolecule has been formed by monomeric units forming a linear chain that has no branches. Even though the chain is called linear, in the solution it tangles up into a spherical cluster resembling a ball of string. The ball's radius depends on the solvent used, because it affects the form the polymer will take in the solution, and to what extent the solvent penetrates or sticks onto the polymer. Determining the

Table 1: Mark-Houwink parameters for different polymeric solutions

Polymer	Solvent	$K[\frac{cm^3}{g}]$	a	temperature $[^oC]$
Styrofoam	benzene	$9,5 \times 10^{-3}$	0,74	25
Styrofoam	toluene	$3,8 \times 10^{-5}$	0,63	25
Styrofoam	decalin	$5,68 \times 10^{-4}$	0,523	20
Polyisobuthylene	benzene	$8,3 \times 10^{-2}$	0,50	23
Polymethyl metacrylate (PMMA)	benzene	$0,94 \times 10^{-5}$	0,76	25
Polyvinyl chloride (PVC)	cyclohexanone	$0,11 \times 10^{-5}$	1,0	25
Cellulose acetate	acetone	$1,49 \times 10^{-5}$	0,82	25
Polyvinyl alcohol[1]	water	0,02	1,0	25
Polyvinyl alcohol[2]	water	0,30	1,0	25
Polyvinyl alcohol[3]	water	0,14	0,60	25
countless proteins	guaninide HCl + $HSCH_2CH_2OH$	$7,2 \times 10^{-3}$	0,66	-
[1]$M = (0,6 - 2,1) \times 10^4$				
[2]$M = (0,9 - 17) \times 10^4$				
[3]$M = (1 - 7) \times 10^4$				

radius is made difficult by the fact that the polymer in the solution is not necessarily spherical, but it can also be flattened from its "poles" or formed distorted in some other way. Another problem in the measurements is that the polymer chain length varies. Solutions in which the polymers aren't homogenic (monodisperse), but instead have a distribution of different molecular masses, are called polydisperse solutions. The viscosity of a polydisperse polymer solution depicts the mean of the polymer's molecular masses and sizes.

Measuring the viscosity gives out the polymer's viscosity-averaged molecular mass M_v. This differs from the averaged-amount-of-substance determined molecular mass M_n, which can be determined for example by measuring the osmotic pressure of the polymer solution. It has been shown that for a polyvinyl alcohol dissolved in water in 25^oC, the ratio of these two molecular masses is
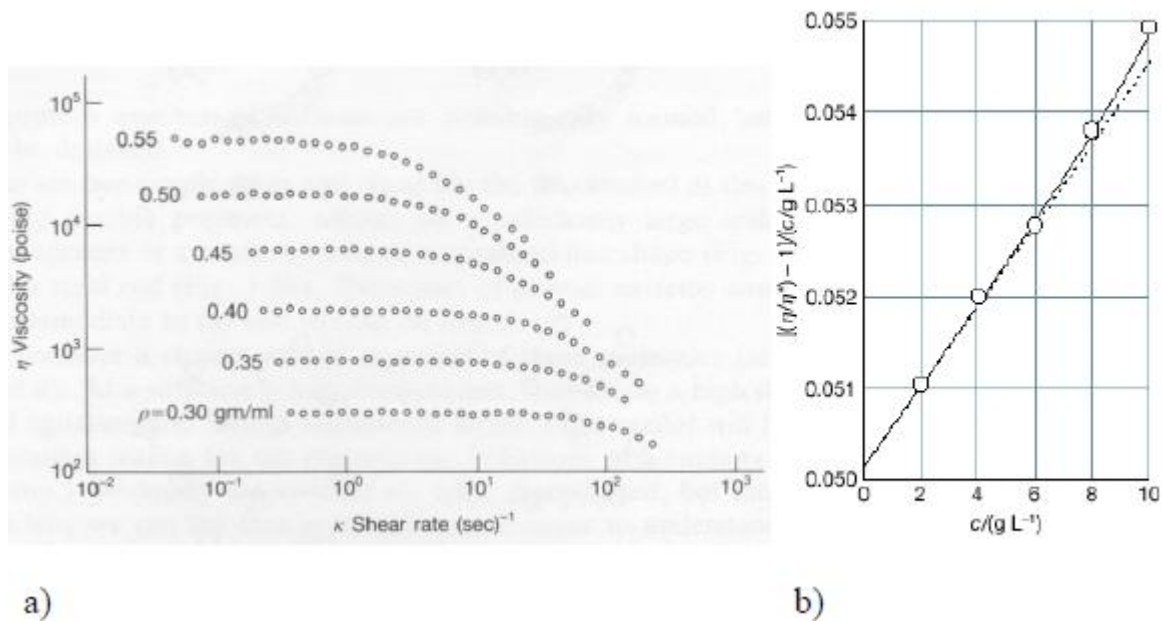
$$\frac{M_v}{M_n} = 1.89. \tag{9}$$

Figure 3: *a) A typical concentration dependence for a styrofoam's specific viscosity ($M_{styr} = 4,11 \times 10^5 \frac{g}{mol}$, solvent N-buthyl benzene). b) Determining the limiting viscosity from data, which can be done by extrapolating the linear fit of the data points to a concentration of zero ($c = 0$).*

2.5 Measuring viscosity with the capillary viscometer

In a capillary viscometer the solution is driven with a pressure difference through a thin cylinder capillary. In measuring the viscosity, the flow of the solution must be laminary. In a laminar flow the flow lines are parallel, and the flow profile is parabolic in that the molecular velocity gets smaller when closer to the capillary walls. It is called a turbulent flow if there are swirls or vortices in the flow. Characteristic for a flow is the Reynold value R.

$$R = \frac{dv\rho}{\eta},\tag{10}$$

where v is the mean velocity of the substance, d the diameter of the capillary and ρ the density of the fluid.

When $R < 100$, the flow is usually laminar. For a Newtonian fluid, the stream velocity is described by Poisseule's equation

$$\frac{dV}{dt} = \frac{\pi r^4 (p - p_o)}{8\eta(x - x_0)}, \tag{11}$$

where η is the viscosity coefficient, and V the volume of the fluid that flows through a straight tube with a radius r in a time unit. The fluid in the tube is driven by the pressure difference $(p - p_0)$ through the distance $(x - x_0)$ (the length of the tube). In this laboratory work, an Ostwald-type capillary viscometer is used. The driving force in the capillary is gravity and therefore the pressure difference is proportional to the fluid density ρ:

$$p - p_0 = \rho g(x - x_0). \tag{12}$$

For the viscosity coefficient, after integrating equation 11

$$\eta = \frac{\pi r^4 g}{8V} \rho t, \tag{13}$$

where V is the volume flown in time t. This equation is valid for ideal capillaries, and can be more generally written as

$$\eta = C\rho t, \tag{14}$$

where C is a constant characterized by the measuring arrangement used, depending on the properties of the capillary, such as diameter, for example. The arrangement constant is defined for each capillary by calibrating it with liquids with known viscosities. In extremely sensitive measurements, a correction term caused by the momentum of the moving liquid, the so called kinetic energy correction term must be added into equations 13 and 14.

When measuring the limiting viscosity needed for the determination of the molecular mass, the relative viscosity η_{rel} gotten from equation 14 can be used.

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}, \tag{15}$$

and from this the specific viscosity

$$\eta_{sp} = \eta_{rel} - 1. \tag{16}$$

When it is known that

$$[\eta] = lim_{c \to 0} \frac{\eta_{sp}}{c}, \tag{17}$$

the limiting viscosity can be determined from a plot of $\frac{\eta_{sp}}{c}$ against concentration, at $c = 0$.

3 Experimental methods

In this laboratory work, a polyvinyl chloride is dissolved into water and its viscosity-averaged molecular mass M_v is determined at $T = 298\ K$. Determining the molecular mass is done by measuring the viscosities of differingly concentrated polyvinyl alcohol (PVOH) solutions with the Ostwald viscometer, where the solution is driven by gravity through a thin capillary.

3.1 Preparations

Heat the thermostatic bath to 298 K. Rinse the viscometer first with water and then acetone. Before measurements, let the acetone vapourize out of the viscometer. Because the PVOH tends to stick on glass surfaces, all glass equipment must be washed with water and acetone, as previously, **before every measurement**. Attach the viscometer from its wider tube vertically into the bath with frame support and clamps. The lines in the narrower part of the tube (where the measurement is done) must be underwater.

The basic solution, a 5 $\frac{g}{dm^3}$ PVOH solution can be found in the reagent cupboard. Filter the needed amount of it through filtering paper and dilute the solutions for measurements from the filtered basic solution. The concentrations for the dilutions are 1, 1.5, 2, 2.5, 3, 3.5, 4 and 5 $\frac{g}{dm^3}$. The dilutions should be mixed thoroughly, but carefully, to avoid foaming.

3.2 Measurements

First measure the flow time of ion exchanged water. Pipette 2 ml of water into the viscometer's wider tube. Let the water in the viscometer temper into 298 K and lift the surface of the water in the narrower tube above the upper line with a pump. Remove the pump and measure the time it takes for the water to cross the path between the two marked lines. Repeat the measurement three times.

Repeat the same procedure for every solution, starting from the most dilute one. Do three repeats for every solution. After measurements, clean the viscometer with acetone and measure the flow time of water. If it's greater than before the PVOH measurements, clean the equipment until the flow time is equal to that of before the measurements.

4   Analysis and report

Determine the PVOH solution's viscosity-averaged molecular mass through equations 15-17 and by assuming that in dilute solutions $\rho_{water} \approx \rho_{PVOH}$. Errors must be included and calculated using basic error propagation laws. As an appendix, a figure of a plot from which the viscosity was determined must be added (a similar picture can be found in Atkins' book). Compare the molecular mass you have determined to the approximate one given on the side of the basic solution bottle. Discuss possible deviations and error. Why is the molecular mass determined so indirectly, in a "difficult" way?

References

[1] Atkins P.W., de Paula J., *Physical Chemistry*, 8th Edition (7th), Oxford University Press, pages XXXX (7th Ed.: pages 748-750).

[2] Halpern A.M. *Experimental Physical Chemistry* 2nd Edition, Prentice Hall, London **1997**, pages 295-299, 493-504.