Determination of the molecular weight of a polymer from intrinsic viscosity measurements (Item No.: P3010601)
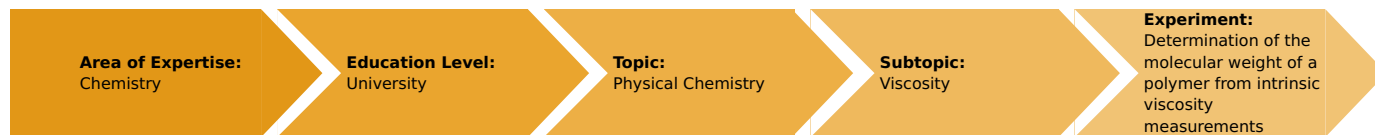
Curricular Relevance

Area of Expertise: Chemistry	Education Level: University	Topic: Physical Chemistry	Subtopic: Viscosity	Experiment: Determination of the molecular weight of a polymer from intrinsic viscosity measurements

Difficulty	Preparation Time	Execution Time	Recommended Group Size
Difficult	10 Minutes	20 Minutes	2 Students

Additional Requirements:

- Analytical balance, 120 g / 0.1 mg

Experiment Variations:

Keywords:

viscosity of liquids, Ostwald capillary viscometer, Poiseuille's equation, macromolecules, mass average and number average molecular weights, Mark-Houwink equation

Overview

Short description

Principle

The viscosity of a liquid is effectively determined by the strength of the intermolecular attractive forces. In the case of solutions, the viscosity of the solvent can alter significantly depending on the type and concentration of the solute. Due to their size, macromolecules have a very considerable impact on the viscosity of the solvent. Viscosity measurements can be used to estimate the mean molecular mass of a macromolecule if something is known about its conformation.

Fig. 1: Experimental set-up

Safety instructions

Acetone
H225: Highly flammable liquid and vapour
H319: Causes serious eye irritation
H336: May cause drowsiness or dizziness
EUH066: Repeated exposure may cause skin dryness or cracking
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P240: Ground/bond container and receiving equipment

Nitric acid, 65%
H272: May intensify fire; oxidizer
H290: May be corrosive to metals
H314: Causes severe skin burns and eye damage
EUH071: Corrosive to the respiratory tract
P280: Wear protective gloves/protective clothing/eye protection/face protection

Hydrochloric acid, 37%
H290: May be corrosive to metals
H314: Causes severe skin burns and eye damage
H335: May cause respiratory irritation
P280: Wear protective gloves/protective clothing/eye protection/face protection

Toluene
H225: Highly flammable liquid and vapour
H361d: Suspected of damaging the unborn child
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P240: Ground/bond container and receiving equipment

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Equipment

Position No.	Material	Order No.	Quantity
1	Immersion thermostat Alpha A, 230 V	08493-93	1
2	Bath for thermostat, makrolon	08487-02	1
3	External circulation set for thermostat Alpha A	08493-02	1
4	Retort stand, h = 750 mm	37694-00	1
5	Right angle boss-head clamp	37697-00	1
6	Universal clamp	37715-00	1
7	Ubbelohde viscosimeter, 0.4 mm	03102-03	1
8	Stopwatch, digital, 1/100 s	03071-01	1
9	Weighing dishes, square shape, 84 x 84 x 24 mm, 25 pcs.	45019-25	1
10	Volumetric flask 250 ml, IGJ14/23	36550-00	1
11	Volumetric flask 100 ml, IGJ12/21	36548-00	4
12	Volumetric pipette, 5 ml	36577-00	6
13	Volumetric pipette, 10 ml	36578-00	1
14	Volumetric pipette, 20 ml	36579-00	1
15	Volumetric pipette, 50 ml	36581-00	1
16	Pipettor	36592-00	1
17	Pipette dish	36589-00	1
18	Funnel, glass, top dia. 80 mm	34459-00	1
19	Water jet pump, plastic	02728-00	1
20	Rubber tubing,vacuum,i.d.6mm	39286-00	2
21	Rubber tubing, i.d. 6 mm	39282-00	4
22	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	4
23	Beaker, high, BORO 3.3, 250 ml	46027-00	4
24	Graduated cylinder 100 ml	36629-00	1
25	Glass rod,boro 3.3,l=200mm, d=5mm	40485-03	1
26	Spoon, special steel	33398-00	1
27	Pasteur pipettes, 250 pcs	36590-00	1
28	Rubber caps, 10 pcs	39275-03	1
29	Wash bottle, plastic, 500 ml	33931-00	1
30	Styropor P, 250 g	48492-25	1
31	Toluene 250 ml	30236-25	3
32	Acetone, chemical pure, 250 ml	30004-25	1
33	Hydrochloric acid 37 %, 1000 ml	30214-70	1
34	Nitric acid , 65% 1000 ml	30213-70	1
35	Water, distilled 5 l	31246-81	1
36	Tubing connector, ID 6-10mm	47516-01	2

Task

Use a thermostatted capillary viscometer to measure the viscosities of solutions of polystyrene in toluene over a range of five polymer concentrations. Determine the intrinsic viscosity and from that estimate the molecular weight (relative molecular mass) of the polymer in this solution.

Set-up and procedure

Set up the experiment as shown in Fig. 1.

Prepare a stock solution (20 mg/ml) of polystyrene in toluene by weighing out 5.000 g of polystyrene, transferring it to a 250 ml volumetric flask and dissolving in toluene. Prepare from this solutions of concentration 16, 12, 8 and 4 mg/ml by transferring 80, 60, 40 or 20 ml respectively of the stock solution to a 100 ml volumetric flask and diluting with toluene up to the mark.

The capillary viscometer must be scrupulously clean. If necessary, clean it with aqua regia, rinse copiously with distilled water and then with acetone. A pipette bulb is useful to draw liquid more rapidly through the capillary arm of the viscometer. To accelerate drying, draw air through the viscometer using a water aspirator pump or, if an oven is available, dry the viscometer at 110 °C.

Mount the viscometer vertically in the constant-temperature bath so that both marks are visible and immersed in the bath. Adjust the thermostat to maintain a temperature of 25 °C ±0.1 °C. Carefully transfer 5 ml of the stock solution to the wider arm of the viscometer and wait ten minutes for thermal equilibration. The solution should be free from bubbles. Place the pipettor over the capillary arm and draw the polymer solution up to a point above the upper mark. Now remove the bulb and record the time taken for the lowest point of the meniscus to pass from the upper to the lower mark. Make three additional measurements using the same solution to attain high precision.

Remove the viscometer and clean it by rinsing it thoroughly four or five times with acetone. Use the pipette bulb to draw or blow the acetone through the capillary arm of the viscometer. Dry the viscometer as described above. Repeat the measurement procedure for each of the other four polymer solutions and finally for 5 ml of the pure solvent.

Theory and evaluation

Viscosity is the resistance a fluid (liquid or gas) offers to flow. It is defined as the force per unit of area required to maintain a unit of speed gradient between two parallel planes spaced a unit of distance apart in the fluid.

In a capillary viscometer the time taken for a fixed volume of liquid to flow through the capillary under the influence of gravity is a function of the viscosity and the dimensions of the viscometer. For a liquid of viscosity η undergoing laminar flow through a capillary tube of radius r and length l under a constant pressure head p, the volume rate of flow of the liquid dV/dt is given by Poisseuille's equation.

$$\frac{dV}{dt} = \frac{\pi \, r^4 \, p}{8 \, \eta \, l} \tag{1}$$

For a particular viscometer, the constants may be put together in A:

$$\frac{dV}{dt} = A \cdot \frac{p}{\eta} \tag{2}$$

At any instant, the pressure head p driving the liquid through the capillary is given by $\rho \cdot g \cdot h$ where ρ is the density of the liquid, g is the acceleration due to gravity and h is the difference in height between the liquid levels in the two arms of the viscometer.

Inverting eq. 2, substituting the expression for the hydrostatic pressure head p and integrating leads to the time required for the liquid to flow from the upper mark h_2 to the lower mark h_1 under the influence of gravity.

$$t = \frac{\eta}{A \, \rho \, g} \int_{h_1}^{h_2} \frac{dV}{h} \tag{3}$$

If the sample volume in the viscometer does not change the integral in eqn. 3 can be treated as a constant. Collecting the constant terms in eqn. 3 and rearranging the following is obtained
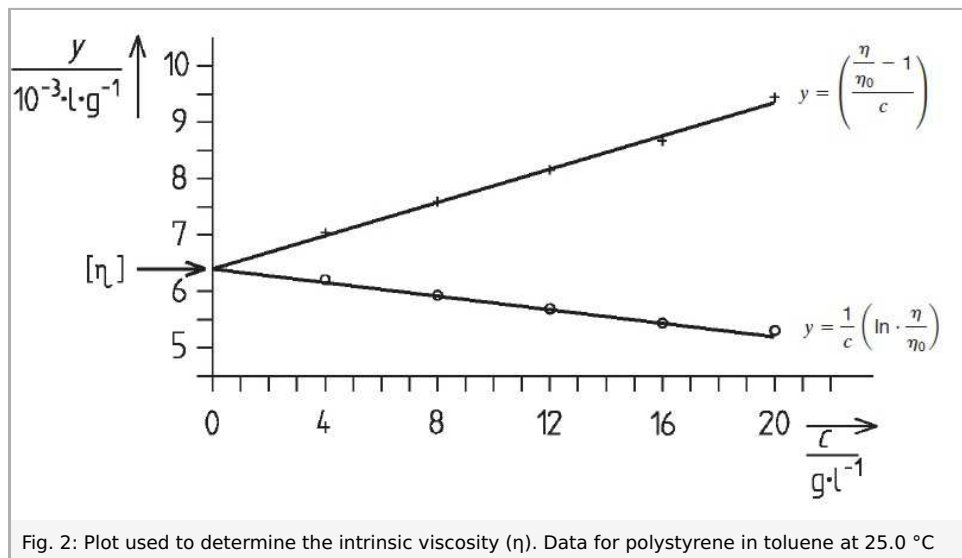
$$\eta = B \cdot \rho \cdot t \tag{4}$$

Fig. 2: Plot used to determine the intrinsic viscosity (η). Data for polystyrene in toluene at 25.0 °C

The relationship between the viscosities η_1 and η_2 of the two liquids 1 and 2 having densities ρ_1 and ρ_2 is

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 \cdot t_1}{\rho_2 \cdot t_2} \tag{5}$$

where t_1 and t_2 are the respective flow times. By calibrating the viscometer under identical experimental conditions with a liquid of known viscosity and density, the viscosity of an unknown sample may be determined directly from Eqn. 5. In the present experiment, Eqn. 5 may be written as

$$\frac{\eta}{\eta_0} = \frac{\rho \cdot t}{\rho_0 \cdot t_0} \tag{6}$$

where the unindexed variables refer to the polymer solution and the index '0' refers to the pure solvent. With the concentrations used here the densities of the dilute polymer solutions and the pure solvent may be taken to be the same and Eqn. 6 reduces to

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{7}$$

At low concentrations the viscosity of a polymer solution is related to the viscosity of the pure solvent by

$$\eta = \eta_0 (1 + [\eta] \cdot c + \dots) \tag{8}$$

where c is the weight concentration of polymer and the term $[\eta]$ is known as the intrinsic viscosity. The intrinsic viscosity may be measured by taking the limit

$$[\eta] = \lim_{c \to 0} \left[\frac{\frac{\eta}{\eta_0} - 1}{c} \right] \tag{9}$$

The experimentally determined ratios η/η_0 (=t/t_0) at various concentrations c are used to plot $[(\eta/\eta_0)-1]/c$ vs. c and to determine the intrinsic viscosity by extrapolating to $c=0$.

If $\eta \approx \eta_0$ it can be shown that $\ln(\eta/\eta_0) = (\eta/\eta_0)-1$. $[\eta]$ may be also determined from the limiting behaviour of $(1/c) \cdot \ln(\eta/\eta_0)$ as c S 0. Plotting both functions enables the intrinsic viscosity to be obtained with greater precision. The value of $[\eta]$ determined from Fig. 2 is 0.0644 l·g^{-1}.

The intrinsic viscosity may be regarded as a measure of the magnitude of the solute-solvent attractive interaction. Often intrinsic viscosity data are interpreted in terms of the empirical Mark-Houwink equation which relates $[\eta]$ to both the shape and the molecular weight of the macromolecular solute.

$$[\eta] = K \cdot M^a$$

M Molecular weight of the macromolecule
K, a Empirical parameters characteristic of a particular solute-solvent pair

The exponent a is sensitive to the shape of the solute and varies from about 0.5, for well-coiled polymer molecules in a poor solvent (due to weak solute-solvent interaction), to nearly 2 for rigidly extended 'rod-like' polymers.

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Data and results

For polystyrene in toluene at 25 °C:

$$K = 3.80 \cdot 10^{-5}\, l \cdot g^{-1}$$

$$a = 0.63$$

Substituting these values and the value of [η] determined above in eqn. 10 results in a value of $133500 = 1.3 \cdot 10^5$ for the average molecular weight of polystyrene in toluene at this temperature.

Table 1

Polymer concentration c/mg·ml^{-1}	Time flow t/s	$\frac{\eta}{\eta_0} = \frac{t}{t_0}$	$\left(\frac{\frac{\eta}{\eta_0} - 1}{c} \right)/l \cdot g^{-1}$	$\frac{1}{c} \cdot \ln\left(\frac{\eta}{\eta_0} \right)/l \cdot g^{-1}$
Pure toluene	76.0 (t_0	1.000	0.000	0.000
20	219.6	2.889	$9.445 \cdot 10^{-3}$	$5.304 \cdot 10^{-3}$
16	181.4	2.387	$8.669 \cdot 10^{-3}$	$5.438 \cdot 10^{-3}$
12	150.4	1.979	$8.158 \cdot 10^{-3}$	$5.688 \cdot 10^{-3}$
8	122.1	1.607	$7.588 \cdot 10^{-3}$	$5.930 \cdot 10^{-3}$
4	97.4	1.282	$7.039 \cdot 10^{-3}$	$6.210 \cdot 10^{-3}$

Quoted flow times are the mean averages of four measurements (Temperature: 25.0 °C).