VISCOSITY MEASUREMENT – MEAN MOLECULAR MASS DETERMINATION

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Task 11

VISCOSITY MEASUREMENT – MEAN MOLECULAR MASS DETERMINATION

I. Aim of the task

The purpose of the task is to collect basic information and master practical skills considering liquids viscosity measurements using a capillary viscosimeter, and calculation of polymer mean visicimetric molar mass.

II. Introduction

1. Definition of viscosity.
2. Newton's formula.
3. Viscosity units.
4. Capillary liquid flow – Poisuille Law.
5. Influence of temperature and concentration.
6. Methods of liquids viscosity measurements.

References:

1. P.W. Atkins, *Physical Chemistry,* 4th edition, Oxford University Press, 1992, 665-667.
2. A.W. Adamson, *Physical Chemistry of Surfaces*, 6th edition, Interscience Publication, New York, 1990, 218-225
3. A.P.H. Peters, *Concise Chemical Thermodynamics*, 3rd edition, CRC Press, 2010, 152-158
4. D.W. Rogers, *Concise Physical Chemistry*, Wiley, 2011 p. 169-170
5. D.T. Haynie, *Biological Thermodynamics*, Cambridge University Press, 2001, 212-214
6. H. Kuhn, H-D. Försterling, D.H. Waldeck, *Principles of Physical Chemistry*, 2nd edition, Wiley, 2009
7. P.W. Atkins, J. de Paula, *Physical Chemistry for the Life Sciences*, 2nd edition, Oxford University Press, 2011, 300-304
8. R. Chang, Physical Chemistry for the Biosciences, University Science Books, 2005
9. R.M. Metzger, *The Physical Chemist's Toolbox,* Wiley, 2012
10. http://www.viscopedia.com/methods/measuring-principles/
11. http://www.machinerylubrication.com/Read/294/absolute-kinematic-viscosity
12. http://www.keywordpicture.com/keyword/capillary%20viscometer
13. http://plc.cwru.edu/tutorial/enhanced/lab/visco/intro/intro.htm

III. Theory

III. 1. Definition of viscosity

Viscosity is the substance property (in all states of matter), describing resistance of medium against its floating under the influence of external forces. The resistance depends on molecular interaction forces in given liquid and thermal oscillations of molecules which reveals as viscosity presence. Its value depends on temperature and velocity of liquid deformation. Quantitatively, viscosity is described as the viscosity coefficient η (named **dynamic viscosity**) present in internal friction (Newton's) law.

"The internal friction force is proportional to the surface and velocity gradient of liquid ${}^{dv}\!/_{dx}$ perpendicular to displacement direction, and it is characteristic of a given fluid", as depicted in Fig. 1.

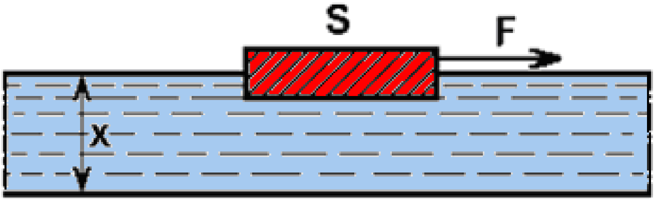

Fig. 1. Applied model of dynamic viscosity.

In a given experiment, there is a fluid in a vessel and the plate whose surface equals S and it floats in the liquid medium. In the same direction (parallel to the liquid surface) two forces are applied: one makes the plate move, the other – resistance force which counteracts this movement. Their values are identical, thus the plate moves with the constant velocity. The resistance force is proportional to the velocity of plate and the area of plate surface contacting with the fluid, and reciprocally to the distance between the plate and the bottom of the vessel x. Eq. (1) presents the formula describing that force:

$$F = \eta \cdot S \cdot \frac{v}{x} \tag{1}$$

where η is the constant factor.

There are molecular interaction forces present between the plate and the liquid and between the liquid and the bottom of the vessel, thus it can be assumed that the velocity of the liquid layer in the vicinity of the bottom equals zero, and the upper layer in the vicinity of the plate equals v – the liquid moves with the same velocity as the plate. Moreover it can be stated that the solid-liquid interactions in the interfacial area are stronger than the liquid-liquid interactions in the bulk.

For very small increments eq. (1) can be transformed to eq. (2):

$$F = \eta \cdot S \cdot \frac{\partial v}{\partial x} \tag{2}$$

where F is the value of mutual interaction force of two parallel layers of fluid (contact tension), S is the area of that layers, $\partial v / \partial x$ is the difference of the laminar flow velocity to distance between the fluid layers ratio.

The law is applicable for laminar flow and does not work in the case of polymer solutions. The unit of dynamic viscosity is [Pa s]. The very common problem described in literature is the flow of the liquid across the pipe, which is presented in Fig 2.

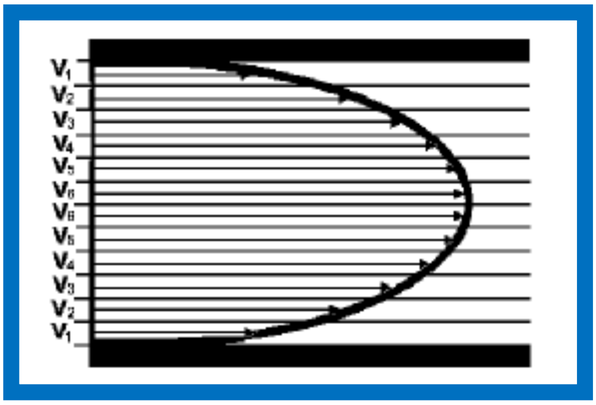

Fig. 2. The linear velocity distribution of liquid flowing across the pipe.

The thin layer of fluid adhering to the pipe wall reminds unmoved. The next layer meets the resistance coming from the immobilised layer. Analogical situation occurs between successive layers placed closer to the middle of the pipe. As it can be seen in Fig. 2, the highest velocity is reached in the area closest to the axis of pipe. The laminar liquid flow through the horizontal pipe is described by the Poisuelle law:

$$Q = \frac{\pi}{8} \cdot \frac{\Delta p}{l} \cdot \frac{r^4}{\eta} \tag{3}$$

where Q – the flow intensity, l – the pipe length, r – the pipe (capillary) radius, Δp – the pressure difference between the ends of pipe.

Along with the temperature growth density of liquid decreases because liquid volume increases and as a result the distances between molecules increase. The values of mutual interaction forces also decrease.

The dependence of viscosity versus the temperature is described by the empirical equation:

$$\log(\eta) = \frac{A}{T} + B \tag{4}$$

where A and B are the constant quantities.

The instrument for liquid viscosity measurements is called ***viscosimeter*****.** The most popular viscosimeters work based on the measurements of:

- pressure drop in capillary
- interaction force between falling ball and liquid (Stoke's method, Höpler viscosimeter, see Fig.3),

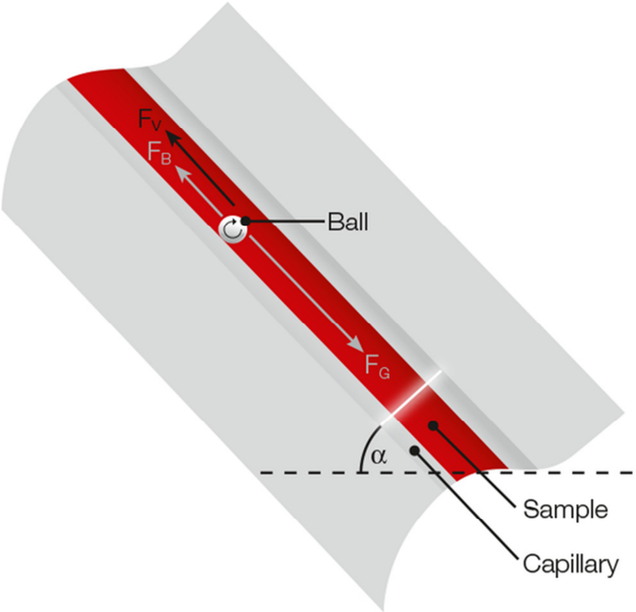

Fig. 3. Rolling ball viscosimeter [10].

- interaction forces between rotating and stationary cylinder (***rheomethers***). The viscosity, in this case, is proportional to the moment induced in the static cylinder when the rotation speed of the second cylinder is constant (Fig. 4).

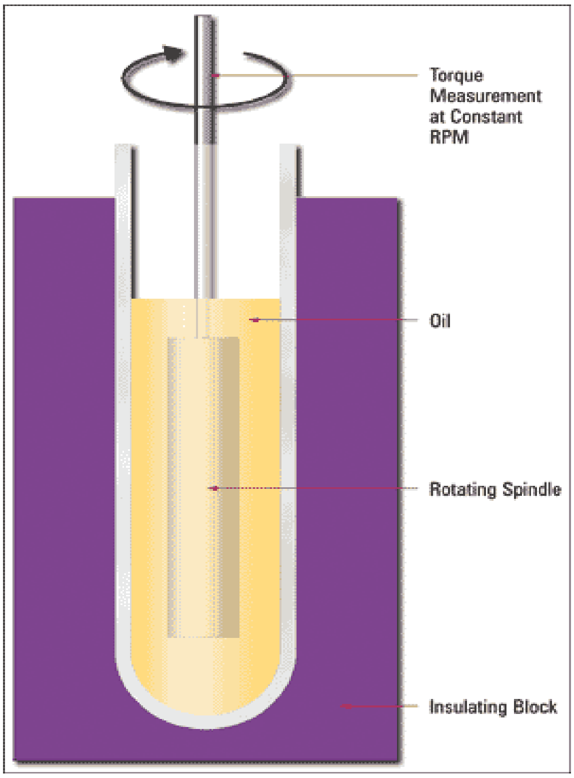

Fig. 4. Rotary viscosimeter [11].

Specific viscosity (kinematic viscosity) is defined by the quotient:

$$\nu = \frac{\eta}{\rho} \tag{5}$$

where ρ is the substance density. The unit of specific density is [m^2/s] .

Relative viscosity is defined as the ratio of the investigated liquid viscosity divided by the viscosity of reference liquid which is known (e.g. water):

$$\eta_{rel} = \frac{\eta_x}{\eta_0} \quad (T=const) \tag{6}$$

where T is the temperature.

Using the Ostwald's capillary viscosimeter (Fig. 5) the viscosity is the time of flow of specified liquid volume through the properly calibrated capillary tube.

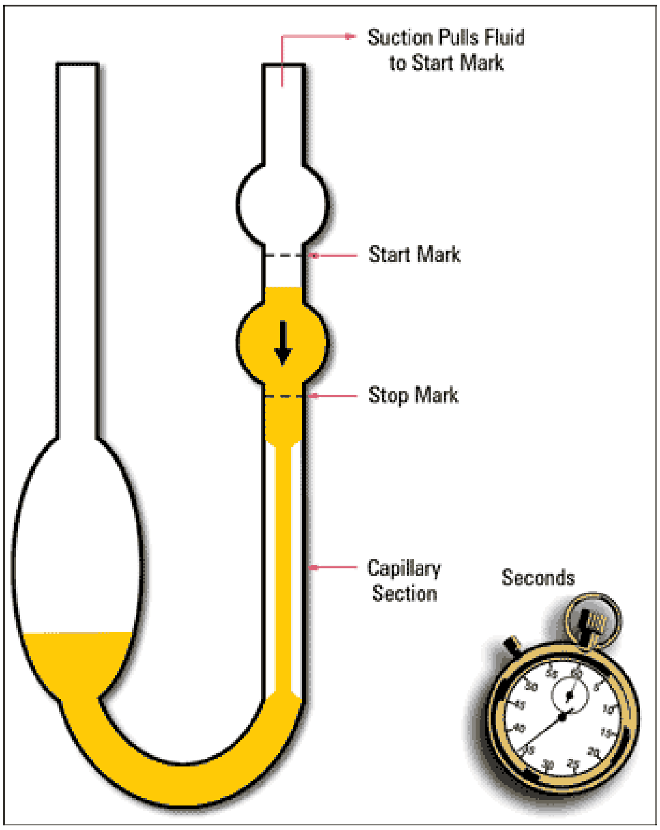

Fig. 5. Ostwald's capillary viscosimeter [12].

The liquid viscosity values are in the range 0.001- 0.0001 Pa s. It is of the order of 0.00001 Pa s, and it is very high in the case of solids.

Knowing the viscosity of the reference liquid we can determine the viscosity of the investigated liquid:

$$\eta_{rel} = \frac{\eta_x}{\eta_0} = \frac{\rho_x t_x}{\rho_0 t_0} \tag{7}$$

For dilute solutions it is usually assumed that the densities of both solutions are equal $\rho_x = \rho_0$ and equation (7) can be written in a simplified form:

$$\eta_{rel} = \frac{t_x}{t_0} \tag{8}$$

where t_x and t_0 are the times of flow of the same volumes of investigated and reference liquids, respectively.

In the case of simple electrolyte solutions, one can calculate viscosity using the formula:

$$\eta = \eta_0 \left(1 + A\sqrt{c}\right) \tag{9}$$

where: n – the solvent viscosity, A – the constant, which is the function of mobility and valence of both types of ions, temperature, constant dielectric and solvent viscosity.

In the electrolyte solutions the influence of interionic forces on viscosity is clearly emphasised. During the flow of the electrolyte solution through the horizontally angled capillary, perpendicular velocity gradient occurs. As a result, velocity of ions varies (Fig. 2), which causes additional deformation of ion cloud. In turn, this causes additional friction between liquid films moving with different velocity.

That is why, in the case of electrolyte aqueous solution, viscosity square dependence on solution molality m has been found:

$$\eta = a \cdot m^2 + b \tag{10}$$

where: a and b are the constant values.

IV. Experimental

A. Devices and materials

1. Devices:

- Ostwald's viscometer with a water jacket
- ultrathermostat
- volumetric flasks: 25 cm^3 – 5 u
- graduated pipettes: 1 cm^3 (1 u), 5 cm^3 (1 u), 10 cm^3 (1 u), 25 cm^3 (1 u)
- graduated cylinders: 10 cm^3 (1 u), 25 cm^3 (1 u)
- beakers 100 cm^3 (1 u), 250 cm^3 (1 u)
- funnel
- chronograph.

2. Reagents:

- chloroformic methyl polymethacrylate solution (concentration 6 g/dm^3),
- chloroform p.a.

B. Preparation of the thermostat for the measurements

- turn on thermostat power supply using electric energy,
- set moderate flow of cooling water,
- check a given temperature on the control thermometer (30°C).

C. Preparation of solutions

Make 0.1, 0.2, 0.3, 0.4, and 0.5 g/100 cm^3 concentrations of working solutions in volumetric flasks (25 cm^3) from the stock solution with chloroform dilution.

D. The measurements

- viscometer should be purged with the use of chloroform before taking measurements;
- with the use of funnel pour 8 cm^3 of the investigated solution into the viscometer;
- wait approximately 10 minutes for the liquid to heat to proper temperature;
- with the use of rubber filler lift the liquid in the capillary above the upper tank;
- measure liquid free flow time between the upper mark (start mark) and the lower mark (stop mark, Fig. 5) over capillary. Each measurement must be taken 3 times;
- as the first liquid there must be used a pure solvent (chloroform), then chloroformic methyl polymethacrylate solutions from the lowest to the maximum concentration;
- before each measurement (change of solution concentration) the viscometer must be purged with the investigated solution;
- when measurements are over, purge the viscometer **twice** using chloroform, then leave such an amount of chloroform in it so as to have the capillary filled;

– solutions after measuring viscosity and chloroform after purging viscometer pour into bottles with the **WASTE** label on them (they are under fume cupboard).

E. Results and conclusions

Put the measurement results in **Table 1**:

Table 1.

	Concentration g/100cm^3						**Measurement number**
	0.0	0.1	0.2	0.3	0.4	0.5	
Time of outflow *t* [s]							**I**
							II
							III
Mean							

where:
η is the solution viscosity,
η_0 is the solvent viscosity,
t_0 is the solvent out flow time,
t is the working solution out flow time,
c is the polymethacrylate concentration in g/100cm^3 of chloroform.

For all investigated solutions calculate:

relative viscosity:

$$\eta_{rel} = \frac{\eta}{\eta_0} \qquad (11)$$

proper viscosity:

$$\eta_{prop} = \eta_{rel} - 1 \qquad (12)$$

and **reduced viscosity**:

$$\eta_{red} = \frac{\eta_{prop}}{c} \qquad (13)$$

Put the obtained values in Table 2:

Table 2.

Viscosity	**Concentration g/100 cm^3**				
	0.1	0.2	0.3	0.4	0.5
relative η_{rel}					
proper η_{prop}					
reduced η_{red}					

Draw the experimental dependence:

$$\eta_{red} = \frac{\eta_{prop}}{c} = f(c) \tag{14}$$

and calculate in a graphical way **the intrinsic viscosity** $[\eta]$, which equals:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{prop}}{c} \tag{15}$$

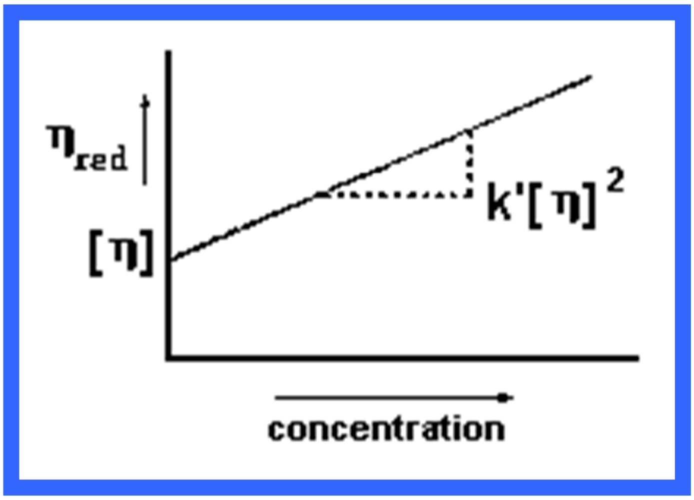

Fig. 6. Intrinsic viscosity determination method [13].

Calculate mean molar mass, $\overline{M}$ of methyl polymethacrylate using the formula:

$$[\eta] = K \cdot (\overline{M})^{\alpha} \tag{16}$$

assuming that for this system at the temperature of 30°C α and K are: $\alpha = 0.8$ and $K = 0.49 \cdot 10^{-4}$.

Calculate the number of mers, *P*, in the methyl polymethacrylate molecule assuming that every mer has an equal weight.

$$P = \frac{\overline{M}}{100} \tag{17}$$