Exercise 7

Investigation of the dependence of liquid viscosity on temperature

Theory:

Definition of viscosity; Types of viscosity; Viscosity of gases and liquids; Dependence of viscosity on temperature; Viscosity measurement methods; Intermolecular van der Waals forces; Hydrogen bonds.

In a Newtonian fluid that is in the state of laminar flow, there are a number of layers that move relative to each other. The layer adjacent to the vessel walls remains stationary, and the speed of subsequent layers changes linearly with the distance (*z*) from the wall. When molecules of the liquid continually move between layers, they transfer the x component of momentum they had in the previous layer. Therefore, if particles move from a slower layer, a layer they move to slows down, and if they come from a faster moving layer, they cause the acceleration of the layer they passed to. The viscosity of the liquid is therefore the resultant slowing effect resulting from the transfer of momentum between the layers. The viscosity depends on the flux of the *x* component of momentum in the *z* direction. Since the *x* component of momentum is proportional to $\frac{dv_x}{dz}$ (where the v_x is the speed of the molecules in *x* direction), the following equation is true:

$$J(\,x\ component\ of\ the\ momentum) = -\eta\frac{dv_x}{dz} \tag{1}$$

Viscosity (viscosity coefficient) is the proportionality constant η in equation (1). The SI unit of viscosity is kg·m^{-1}·s^{-1}, but is often expressed in poises (1 P= 10^{-1} kg·m^{-1}·s^{-1}).

For gases, assuming equal density, the flux of the *x* component of momentum in the *z* direction (J_z) is equal:

$$J_z = -\frac{1}{2}v_{mean}\lambda mN\left(\frac{dv_x}{dz}\right)_0 \tag{2}$$

Where v_{mean} - mean speed, λ- mean free path, *m*- mass, *N*- numerical density of molecules (in number·m^{-3} unit).

To take into account possible collisions with other molecules that occur when molecules travel a long distance, expression (2) should be multiplied by the coefficient $\frac{2}{3}$. Combining equations (1) and (2) we obtain the expression for the viscosity coefficient of gases:

$$\eta = \frac{1}{3}v_{mean}\lambda mN \tag{3}$$

Because $v_{mean} \propto T^{1/2}$, as the temperature increases, the viscosity of gases increases. However, the viscosity of a liquid decreases with increasing temperature because it helps overcome intermolecular interactions. The dependence of the viscosity of a liquid on temperature can be expressed by an empirical Arrhenius–Gutzmann formula:

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

where *A, B* are constants for a given liquid, *T*- temperature. This equation describes well the behavior of non-polar liquids, but for polar liquids there are significant deviations.

Theoretical considerations on the viscosity of liquids also lead to formula analogous to equation (4). For a molecule in a liquid to move, it must have the energy to break free from neighboring molecules. This minimum energy is called the activation energy for viscous flow (E_a) and is expressed in J·mol^{-1}. The dependence of viscosity of a liquid on temperature, taking into account the activation energy, has the form:

$$\eta = \eta_0 e^{E_a/(RT)} \tag{5}$$

Where η_0 is the initial viscosity, R is the gas constant. Equation (5) is met within a narrow temperature range. Typically, the activation energy is comparable to the average potential energy of intermolecular interactions.

One of the methods used to measure viscosity is based on measuring the speed of a ball of appropriate size and known density falling in a pipe filled with the tested liquid. Let us consider the motion of a rigid ball in a viscous medium. The force of gravity, Q, reduced by the buoyant force, P, acts on a ball in a liquid:

$$Q - P = \frac{4}{3}\pi r^3(\rho_b - \rho_l)g \tag{6}$$

where r – ball radius, ρ_b – ball density, ρ_l– liquid density, g – acceleration of gravity.
Initially, the ball falls with an accelerated motion, but as the falling speed increases, the internal friction force (directed opposite to the direction of movement of the ball) also increases, which eventually balances the force Q-P. Once this balance of forces is achieved, the ball falls at a constant speed. According to Stokes' law, the internal friction force, f, is given by:

$$f = 6\pi\eta r v \tag{7}$$

where r – ball radius, v – ball falling speed, η – viscosity of a liquid. Therefore, when f=Q-P we get:

$$6\pi\eta r v = \frac{4}{3}\pi r^3(\rho_k - \rho_c)g \tag{8}$$

By rearranging equation (8), we obtain an expression that allows us to calculate the viscosity:

$$\eta = \frac{2}{9}\frac{r^2(\rho_k - \rho_c)g}{v} \tag{9}$$

or:

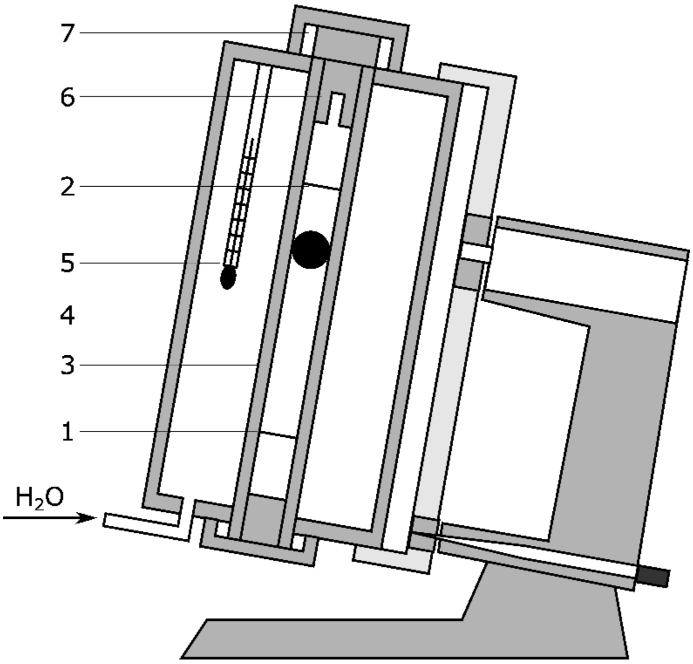
$$\eta = \frac{2}{9}\frac{r^2(\rho_k - \rho_c)gt}{l} \tag{10}$$

where l – the ball's falling path, t – the time needed to travel this distance. This formula is strictly satisfied when the ball slowly falls in an infinite volume of liquid. Therefore, corrections (usually experimental) should be applied, taking into account the influence of the finite length of the ball's falling path. Methods based on measuring the ball's falling speed are mainly used to study viscosity changes. The equation then used is:

$$\eta = K(\rho_k - \rho_c)t \tag{11}$$

where K – ball constant.

A Höppler viscometer (Scheme 1) is used to measure viscosity. To determine the viscosity at a given temperature, the ball's falling time between lines 1 and 2 is measured and formula (11) needs to be used. The internal tube of the Höppler viscometer (3), inclined at an angle of 80° to the horizontal, is placed in the jacket (4), to which water at the desired temperature is supplied from the thermostat. The temperature is read on the thermometer (5) placed in the water jacket. The liquid is poured into the thoroughly washed and rinsed pipe (3) through the upper hole, then a ball is thrown in and the metal cap (6) is inserted. It needs to be done carefully not to introduce air bubbles, which may be a source of errors. Then close the pipe by tightening the nut (7). After filling the Höppler viscometer once, the ball's falling time can be repeatedly measured by rotating the measuring part of the instrument around its axis by 180°.



Scheme 1. Höppler viscometer.

The aim of the exercise:

Investigating the dependence of glycerin viscosity on temperature, determining the constants A and B in the Arrhenius-Gutzmann equation and calculating the activation energy for viscous flow.

Experimental procedure:

Measurements should be made in the temperature range 293-323 K every 5 K using a Höppler viscometer filled with glycerin.

1. Set the desired temperature on the thermostat (the thermostat user manual is located next to the device).
2. Wait 10 minutes for the temperatures to stabilize (until the temperature read on the thermometer located in the water jacket of the viscometer is consistent with the temperature set on the thermostat).
3. Measure the ball's falling time between lines 1 and 2 by rotating the measuring part of the viscometer around the axis by 180°. Take five measurements at each temperature.
4. Place the results of direct readings of the ball's falling time and the calculated mean falling time at a given temperature in the table:

Temperature T [K]	Ball's falling time t [s]	Mean ball's falling time $\bar{t}$ [s]

5. Calculate the viscosity of glycerin for each temperature using formula (11) and taking into account the ball constant $K = 6.71 \cdot 10^{-6}\ m^2 \cdot s^{-2}$, ball density $\rho_b = 7710.3\ kg \cdot m^{-3}$, and glycerin density $\rho_l = 1260\ kg \cdot m^{-3}$ (due to the small change in the density of glycerin in the tested

temperature range, approximately 1%, these changes can be neglected and the density of glycerin determined at room temperature can be used).

6. Calculate the log η and $\frac{1}{T}$ values, and summarize them in a table together with the calculated viscosity values:

T [K]	$\frac{1}{T}$ [K^{-1}]	η [$kg\cdot m^{-1}\cdot s^{-1}$]	log η

7. Plot $\log\eta = f\left(\frac{1}{T}\right)$ and add the regression line on the graph.
8. Calculate the values of constants *A* and *B* and their standard errors using the least squares method.
9. Calculate the activation energy for viscous flow by multiplying the constant *A* by the gas constant (expressed in $J\cdot K^{-1}\cdot mol^{-1}$) and the factor 2.303.