

## 1.a. Determination of viscosity-average molar mass of polymer



The dynamic viscosity  $\eta$  of the liquid can be measured by capillary U-tube type Ubbelohde viscometer (**FIGURE 1**). At this instrumental setup, the following formula is valid:

$$\eta = C \cdot \rho \cdot t \quad (1.1.)$$

where  $C$  is constant of the viscometer (given by manufacturer),  $\rho$  is density of the liquid to be examined, and  $t$  is flow time between upper  $Z_1$  and lower  $Z_2$  level (**FIGURE 1**). At low concentrations, we can approximate the solution density with the density of pure solvent. Strictly isothermal conditions are important for an exact viscosity measurement. The dynamic viscosity of the solutions can be compared with dynamic viscosity of the pure solvent  $\eta_0$ . Thus we obtain relative viscosity:

$$\eta_{rel} = \eta / \eta_0 = t / t_0 \quad (1.2.)$$

where  $t$  and  $t_0$  are the flow times for solution and solvent.

Specific viscosity  $\eta_{sp}$  is given by

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_{rel} - 1 = \frac{t - t_0}{t_0} \quad (1.3.)$$

Reduced viscosity can be calculated as

$$\eta_{red} = \frac{\eta_{sp}}{c} = \frac{t - t_0}{ct_0} \quad (1.4.)$$

At low solute concentration  $c$ , the reduced viscosity  $\eta_{red}$  become important mainly for macromolecules because an extrapolation  $\eta_{red}$  to zero concentration  $c$  gives intrinsic viscosity. It is found that some solutions of macromolecules often fit the Mark-Kuhn-Houwing-Sakurada (MKHS) relationship:

$$\eta^* = K_{\eta^*} \cdot M^a \quad (\text{linear form: } \ln(\eta^*) = \ln(K_{\eta^*}) + a \ln M) \quad (1.5.)$$

where  $K_{\eta^*}$  and  $a$  are constant that depend on temperature, the solvent type, and type of macromolecule.  $M$  is the viscosity-average molar mass of macromolecule. The linear form (1.5.) enables the determination of the MKHS constants using fit of the experimental intrinsic viscosity dependence on known molar mass of monodisperse homologous polymers. The knowledge of MKHS constants  $K_{\eta^*}$  and  $a$  allows for an easy determination of the viscosity-average molar mass of a polymer by measuring the intrinsic viscosity  $\eta^*$ .

The good method for the extrapolation of the intrinsic viscosity  $\eta_{red}$  to  $c = 0$  is to use empirical equations:

$$\frac{\eta_{sp}}{c} = \eta^* + k_1 (\eta^*)^2 c \quad (1.6.)$$

$$\frac{\ln(\eta / \eta_0)}{c} = \eta^* - k_2 (\eta^*)^2 c \quad (1.7.)$$

The intercept and the slope of the each equation we obtain using linear least square regression. The intercepts on y axis are equal to intrinsic viscosity in both equations. The slopes are different but the sum of the constants  $k_1$  and  $k_2$  gives  $\frac{1}{2}$ .

**?** **TASK:** Determine viscosity-average molar mass of polyethylene glycol (PEG) using Ubbelohde viscometer. Find intrinsic viscosity  $\eta^*$  using eqns (1.6.) and (1.7.) and verify empirical relation:  $k_1 + k_2 = 0,5$ . MKHS constants of PEG are  $K_{\eta}^* = 1,05 \cdot 10^{-4} \text{ dm}^3 \text{ g}^{-1}$ ,  $a = 0,570$  at 25-30°C.

**✂** **LABORATORY AIDS AND CHEMICALS:** Ubbelohde viscometer (**FIGURE 1**), thermostatic bath, thermometer, stopwatch, funnel, 2 beakers (50 ml), 2 divided pipettes (10 ml), 1 divided pipettes (5 ml), syringe with thin hosepipe, small stopper, 6 volumetric flasks (50 ml), PEG solution 50 g/dm<sup>3</sup>.

**📄** **INSTRUCTIONS:** Become familiar with the function of the viscometer and thermostatic bath (set temperature to 25°C).

Refill and flush the viscometer's tubes and reservoirs (**FIGURE 1**) by pure water three times at least by means of syringe with thin hosepipe.

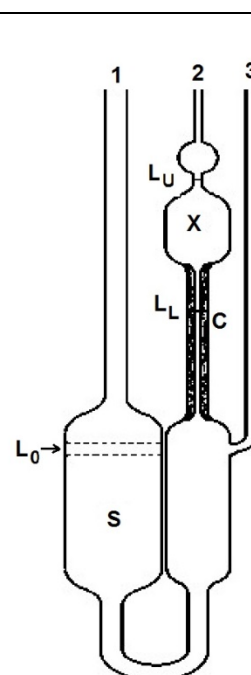
Fill the sample reservoir of the viscometer by pure solvent (water) through filling tube **1** to level  $L_0$ . Close tube **3** with a stopper. Connect tube **2** with syringe. Adjust liquid using syringe to a point about 10mm above level  $L_u$ . Remove syringe and stopper. Measure the flow time taken for the bottom of the meniscus to fall from the upper level mark  $L_u$  to the lower level mark  $L_L$ . Repeat the measurement of the solvent until the difference between the flow times less than 0,25 s.

Prepare water solutions with PEG concentrations: 5, 10, 15, 20, 25 and 30 g/dm<sup>3</sup> in volumetric flasks (note: this sample preparation may start within tempering of the viscometer). Fill viscometer with first sample 5 g/dm<sup>3</sup>. Measure the flow time of the sample three times. Apply the same procedure for more concentrated sample. Cleaning by flushing with water is not necessary with exception for final cleaning.



**REPORT: TABLE 1:** solute concentrations  $c$ , flow times  $t$  (three per solvent as well as for each solution), average flow times, values:  $\eta_{rel}$ ,  $\eta_{sp}$ ,  $\eta_{red}$ , and  $\frac{\ln(\eta/\eta_0)}{c}$ .

**COMMON GRAPH 1:** two dependences:  $\eta_{red}$  and  $\frac{\ln(\eta/\eta_0)}{c}$  on  $c$  (including regression



**FIGURE 1:** Ubbelohde viscometer: **S** ... sample reservoir, **X** ... timing bulb, **C** ... capillary,  $L_U$  and  $L_L$  ... markers of upper and lower level, **1**... filling tube, **2**... capillary tube, **3** ... venting tube.

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lines). **NEXT:** intrinsic viscosity  $\eta^*$  [ $dm^3 g^{-1}$ ], molar mass of PEG in  $g mol^{-1}$  and number of ethylene glycol units. Apply slopes of regression lines, eqn (1.6.), and eqn (1.7.) to verify relation  $k_1 + k_2 = 0,5$ .