Practical No 35

ESTIMATION OF VOLUME AND RADIUS OF A SINGLE MOLECULE APPLYING THE VISCOMETRIC METHOD.

Viscometry is a part of rheology, which focuses on measurements of viscosity of liquids, including solutions. The Einstein formula (1) describes viscosity of the solution in relation to viscosity of the solvent, assuming that molecules of the dissolved substance are spherical.

$$\frac{\eta}{\eta_0} = 1 + 2{,}5\Phi, \text{ where:} \qquad (1)$$

η – viscosity of the solution, η_0 – viscosity of the solvent, Φ – volume coefficient of the solution.

The volume coefficient of the solution defines a ratio of volume of molecules of the dissolved substance (V_s) to total volume of the solution (V_t):

$$\Phi = \frac{V_s}{V_t}. \qquad (2)$$

In case of solutions a widely applied parameter is the specific viscosity (η_{spec}) defined as:

$$\frac{\eta}{\eta_0} - 1 = \eta_{spec} = 2{,}5\Phi \qquad (3)$$

Application of the viscometric method enables estimation of volume of a single molecule of the dissolved substance, using constant numbers to describe the Φ value. The volume of molecules of the dissolved substance (V_s) can be calculated by multiplying the number of moles of the dissolved substance (n) times the Avogadro number (N_A) times the volume of a single molecule (v):

$$V_s = nN_A v. \qquad (4)$$

Total volume of the solution (V_t) can be calculated knowing molecular mass of the dissolved substance (M), number of moles of this substance (n) and concentration of the solution (c). After having re-arranged below-given formulas that define the c and the n (m – mass of the dissolved substance)

$$c = \frac{m}{Vt}, \qquad n = \frac{m}{M}$$

the (V_t) can be calculated:

$$V_t = \frac{nM}{c} \qquad (5)$$

After having substituted the formula (2) by the formulas (4) and (5) one can calculate the volume coefficient of the solution:

$$\Phi = \frac{cN_A v}{M} \tag{6}$$

After having substituted the formula (3) by the formula (6) the following formula is obtained:

$$\eta_{spec} = 2{,}5\frac{cN_A v}{M} \tag{7}$$

After having divided the formula (7) by the c one can define the limiting viscosity number (η_{lim}), as a limit of the quotient (η_{spec}/c), when the c is approaching 0, thus $lim_{c\to 0}\frac{\eta_{spec}}{c}$:

$$\lim_{c\to 0}\frac{\eta_{spec}}{c} = \eta_{lim} = 2{,}5\frac{N_A}{M}v \tag{8}$$

The limiting viscosity number (η_{lim}) is estimated by measurements of the specific viscosity (η_{spec}) of solutions with different concentrations of the examined substance. Obtained results are applied to make a plot of the (η_{spec}/c) against the c. A straight line should be obtained. Then, the line should be extrapolated (prolonged) to the c value equal to 0 (c →0), which corresponds to the value of the η_{lim}. After having estimated the η_{lim} value one can re-arrange the formula (8) to calculate volume of a single molecule (v), and then, assuming that a molecule is a sphere, the radius of a single molecule (r).
Measurements of the η_{spec} are carried out in the Ostwald viscometer. The volume (V) of a viscous liquid flowing through the viscometer capillary having the radius *r* and the length *l* under the pressure change Δp is related to time (t) of a laminar flow according to the Poiseuille equation:

$$V = \frac{\pi r^4 \Delta p}{8l\eta}t, \tag{9}$$

where Δp = ϱgh is a hydrostatic pressure exerted by a column of liquid of the density ϱ and the height h. By re-arranging the equation (9) one can calculate both the (η) and the (η_0):

$$\eta = K\varrho t, \quad \eta_0 = K\varrho_0 t_0 \tag{10}$$

where K is a constant parameter calculated using constant parameters of the viscometer: the *l*, the h, the V and the *r*. By dividing the (η) by the (η_0) one can calculate the relative viscosity (η_{rel}) of a solution:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}\frac{\varrho}{\varrho_0} \tag{11}$$

Where the ϱ stands for the density of a solution and the ϱ_0- density of a solvent.

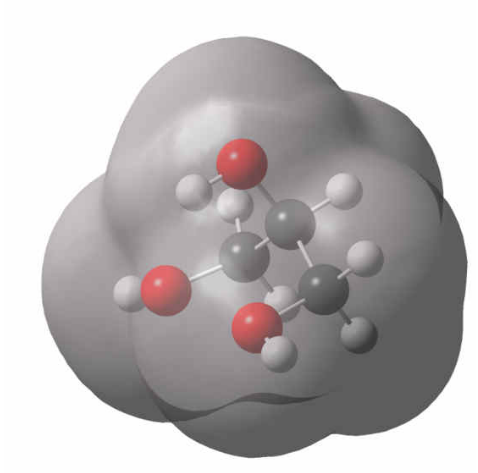

Figure. Geometry of a molecule of glycerol in water environment.

The figure shows geometry of a molecule of glycerol in water environment, calculated applying the calculation packet GAUSSIAN 09, applying the IEFPCM/DFT/6-311++G(d,p) method. Grey transparent outline is a limit of calculated „real" size of the molecule, which is correlated with Van der Waals radii for atoms and the electron density $\leq 0{,}001\frac{electron}{bohr^3}$. The calculated molar volume (V_M) for glycerol is equal to: $V_M = 76{,}762\frac{cm^3}{mol}$. Taking into account the V_M and the Avogadro number, one can calculate the volume v of a single molecule, which is equal to: **v = 127,47 Å^3.**

Required background in theory

1. Types of liquid flow: laminar flow, turbulent flow.
2. Internal friction during transportation of liquids.
3. Viscosity of liquids – Newton law – viscosity coefficient, viscosity units.
4. Which liquids are newtonian and which are non-newtonian ?
5. Poisseuille law for liquid transportation in a vessel
6. Einstein formula describing viscosity of a solution in relation to viscosity of a solvent, in which spherical molecules are dissolved..
7. Define a relative viscosity, specific viscosity and limiting viscosity number.
8. Method of determination of limiting viscosity number.
9. Describe the method of determination of volume and radius of a single molecule using Ostwald viscometer and Poisseuille law.

Literature

1. Glaser, "Biophysics", Springer, 2001.