IONIC MIGRATION VELOCITY

Attention! The text presented below is by no means enough to prepare for the practical. Please refer to recommended literature.

Charged particle present in electric field experiences electric force F_{el} equal to:

$$F_{el} = qE,\tag{1}$$

where q refers to electrostatic charge value while E refers to intensity of electric field. When charged particles are ions, electrostatic charge value can be described by equation:

$$q = z \cdot e, \tag{2}$$

where z refers to ion valency while e refers to elementary charge. Relationship between intensity of electric field E and electric potential U can be presented as:

$$E = \frac{U}{d},\tag{3}$$

where d refers to the distance between the point possessing potential U from the source of electric field. Electric force leads to accelerated motion of a charge in vacuum, while in non-vacuum media this motion is retarded by frictional force F_{op} proportional to the velocity of the charge (ion):

$$\mathbf{F}_{\mathrm{op}} = \boldsymbol{\mu} \cdot \mathbf{v} \tag{4}$$

For spherical objects having radius R and moving in a medium of viscosity η the proportionality factor μ is equal to $6\pi\eta R$. Thus, the formula (4) can be rewritten into Stokes formula (Stokes law):

$$F_{op} = 6\pi\eta R \cdot v \tag{5}$$

According to first law of motion, an ion in solution moves with a constant speed v when $F_{el} = F_{op}$. Thus, the speed of ions in solution is proportional to the intensity of electric field E:

$$\mathbf{v} = \mathbf{u} \cdot \mathbf{E} \tag{6}$$

In formula (6) the proportionality factor u is called ionic mobility (defined as a velocity at which ions move under the electric field intensity of $1 \text{ V} \cdot \text{cm}^{-1}$). Since ionic mobility depends on solution concentration, it is useful to estimate ionic mobility for infinitely diluted solution (u_o). Calculation of u_o allows for determination hydrodynamic radius R of an ion in solution. If an ion moves at constant speed when $F_{el} = F_{op}$, then

$$z \cdot e \cdot E = 6\pi\eta R \cdot v$$
, and therefore $R = \frac{z e}{6\pi\eta u_0}$ (7)

- 1. Velocity of an ion in solution v may be quantified by considering distance Δl travelled by the ion at constant speed versus time Δt .
- 2. Ionic mobility in solution may be calculated from the following formula:

$$u = \frac{\Delta l}{\Delta t} \frac{d}{U},\tag{8}$$

where d refers to the distance between the electrodes, U refers to voltage applied to the electrodes.

- 3. Ionic mobility for infinite dilution (u₀) may be found on the basis of the plot of ionic mobility (u) versus solution concentration (c) by extrapolation of the straight line to zero concentration.
- 4. Hydrodynamic radius of an ion (R) can be calculated using formula (7).